THE MULTIPLE EQUILIBRIUM ANALYSIS MODEL AND ITS APPLICATION TO THE STUDY OF ADSORPTION

By

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Porous solids are used extensively in many adsorbent and separation applications, as well as serving as catalyst supports for many heterogeneously catalyzed reactions. Of the many solids available, most specialty adsorbents are carbon or silica based. Many of the carbonaceous adsorbents are derived from coal and wood chars, as well as being synthetically produced from macrorecticular resins. The siliceous based adsorbents include silica gel and zeolites. Silica, like carbon, is amorphous and provides a distribution of pore sizes capable of adsorbing probe molecules of varying size and shape. Zeolites are crystalline solids, some of which occur naturally while others are synthetically produced. Crystallinity in a solid defines the limitation and application of an adsorbent to effectively adsorb certain molecules while excluding others. Understanding those properties of a solid which favor the adsorption of probe molecules is vital in selecting an adsorbent for the appropriate application.

Currently there are several adsorption models in use, and many under development, which characterize the physical properties of solid adsorbents, namely

surface area and pore size. One of the main challenges facing current adsorption models is the ability to predict adsorption isotherms for new adsorbates based on the known properties of the adsorbate and the adsorbent. Another challenge is the ability of these adsorption models to be applicable to all adsorptives and all adsorbents.

Two commercial carbonaceous adsorbents and two silica based adsorbents are examined for their ability to favorably adsorb selected probe molecules. Examination of the adsorption data by the Multiple Equilibria Analysis (MEA) model has provided great detail about the adsorption process. In an MEA interpretation, multiple adsorption processes are found to contribute to the total adsorption isotherm. These multiple adsorption processes exhibit different adsorption affinities which correspond to the adsorption of probe molecules into pores of different dimensions. In conjunction with equilibrium affinity, capacities for adsorption of a probe molecule can be transformed into accessible surface areas and corresponding pore volumes. Enthalpies of adsorption for the individual processes are calculated from the temperature dependent equilibrium constants. Correlation of the enthalpies and equilibrium constants for the selected probe molecules with the van der Waals [a] parameter is linear for those adsorbates undergoing nonspecific, dispersion interactions. This affords the opportunity of the MEA model to predict enthalpies and equilibrium constants, and in turn the adsorption isotherm, for probes not yet examined.

Extension of the MEA model to liquid-solid adsorption equilibria is described for selected adsorbates with a carbonaceous adsorbent and silica gel. Multiple equilibrium constants are found indicating the presence of more than one adsorption process. For the carbonaceous adsorbent, nonspecific interactions dominate, whereas silica undergoes specific donor-acceptor interactions.

Preliminary results for the synthesis of a silica based acid catalyst and its potential application for the production of methyl tertiary butyl ether (MTBE) are described.

CHAPTER 1
INTRODUCTION

From the early years of our civilization, porous materials have been used for special applications. One of the earliest reported uses dates back approximately 1000 years ago when the Egyptians used carbon to purify drinking water for medicinal purposes.[1] In 1756 Baron A.F. Cronstedt first discovered zeolites, aluminosilicates.[2] He noticed that, when these solids were heated, gases were evolved, and when cooled, they adsorbed approximately the same volume previously lost. In 1777 Fontana noted that freshly calcinated charcoal was capable of adsorbing many times its own volume of various gases.[3] Since these early discoveries, porous materials have been utilized for a wide range of applications including separation and catalytic processes. Understanding the properties that most influence adsorption of an adsorptive by an adsorbent allows for the appropriate selection of materials for adsorbent and catalytic applications.

Of the many adsorbents available, the most commonly used are carbon and silica based. Porous carbonaceous adsorbents are derived from coal, peat, and wood chars, as well as synthetically produced carbons made from macrorecticular resins.[1,4] They are used extensively as adsorbents for the removal of organic contaminants from waste water,[5] in industrial flue gas scrubbers to minimize SO_x and NO_x pollutants,[6] for military decon and demil applications,[7,8] as gas purifiers,[9-11] as a means of storing fuels, fuel cells, and as catalyst supports.

Metal oxides such as silica gel, SiO_2, alumina, Al_2O_3, and zeolites are also used extensively as adsorbents and catalyst supports.[12-14] These solids offer a functionalized surface capable of ion exchange for heavy metal removal from streams and aquifers. Zeolites are recognized as strong solid acids and are used in the petrochemical industry as alkylation, isomerization, and cracking catalysts.[13,15,16]

The solids just mentioned, as well as others, have one thing in common; regardless of their chemical composition, they are porous and they adsorb. However, not all solids adsorb the same way, nor do they adsorb the same things. Silica gel and carbonaceous adsorbents generally have no long range order to their structure and are considered amorphous. Zeolites, unique in their composition, are recognized as being microporous, crystalline solids. Crystallinity in a solid adds a limitation to the size of the adsorptive capable of being adsorbed. This allows zeolites to function as size exclusion adsorbents and catalysts.[14] This feature is not common to amorphous materials where an adsorbate molecule is capable of being adsorbed by a range of pore dimensions. The degree to which a solid adsorbs a particular adsorptive is dependent on the porosity of the solid.

Porosity is a term used to describe a solid's pore size distribution and specific surface area. IUPAC defines pores which are less than 20 Å in diameter as micropores, pores between 20 and 500 Å as mesopores, and pores larger than 500 Å in diameter as macropores.[13,17] Surface area, which is the general physical property used to describe solids in the literature, is a function of pore size. Large quantities of smaller pores afford a large internal surface area, whereas large pores result in a lower surface area.

The process of adsorption can be divided into two areas: chemisorption and physisorption.[18] Chemisorption, in general, is the formation of a chemical bond between the adsorbate and the adsorbent. The enthalpy of adsorption for a chemisorption process is generally greater than 15 kcal $mole^{-1}$. Physisorption, or reversible chemisorption, occurs as a result of the attractive forces between the molecules of the solid and the gaseous or liquid adsorbate. These forces are generally London dispersion forces and dipole-dipole attraction potentials. Dispersion forces are a result of oscillations in the electron cloud of the adsorptive and the adsorbent such that an attraction between the two occurs resulting in adsorption.[19,20] These interactions are weak and occur over short distances, decreasing rapidly with distance (r^{-6}), Figure 1-1. The strength of the physisorption process will depend on several factors, the first being the size and type of pores which are being accessed. For those solids consisting of a range of pore sizes, the narrower the pore diameter the greater the surface contact between the adsorbate and the adsorbent and the greater the enthalpy of interaction,[21] generally 5 to 15 kcal $mole^{-1}$. This was demonstrated by Everett and Powl who calculated adsorption potentials for micropores in carbonaceous adsorbents, assuming slit shaped and cylindrical pore geometry, and compared this to adsorption on a graphitic plane surface.[22] Cylidrical pores were found to experience a greater adsorption potential than slit-shaped pores as a result of greater surface contact. The maximum adsorption potential was found to occur in pores whose diameter closely matched that of the adsorptive, Figure 1-2. As the pore diameter increased, the adsorption potential approached that of a single graphitic surface. This indicates that the energy of adsorption is closely related to the diameter of the adsorbing pore in relation to

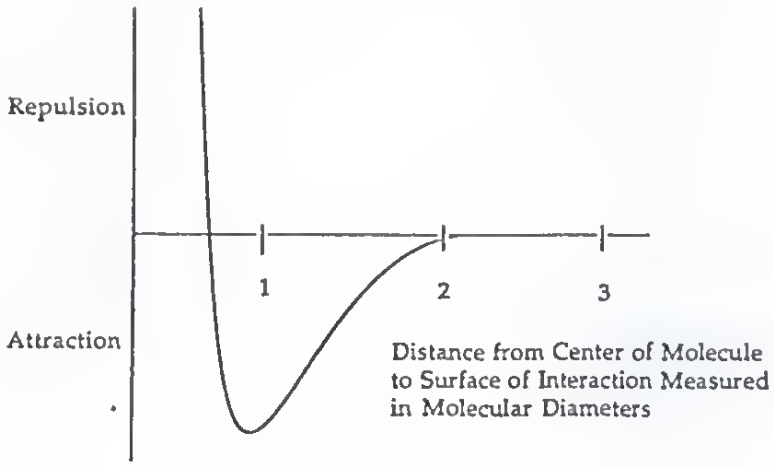

Figure 1-1: van der Waals Attraction at Molecular Dimensions. The attraction between molecules decreases rapidly as the distance between molecules increases.

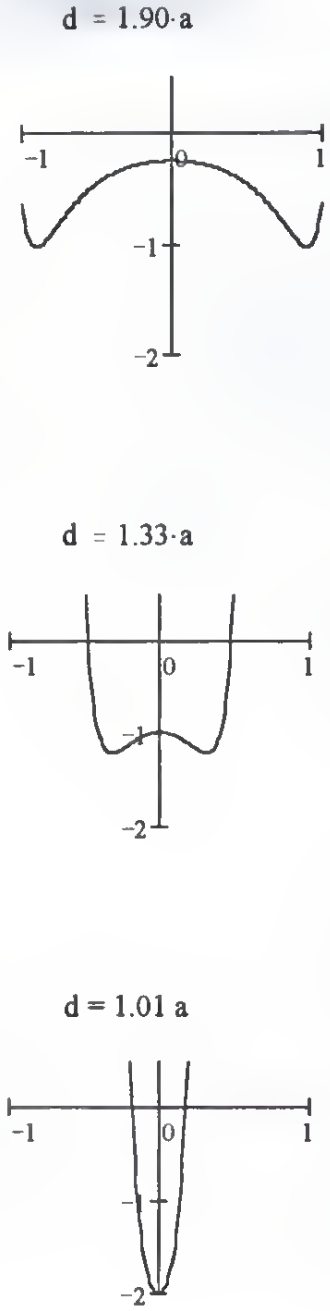

Figure 1-2: Adsorption Potential in Micropores. The narrower the pore diameter the stronger the adsorption potential. Here d is the diameter of the pore and a is the size of the adsorptive.

the size of the adsorptive. As the pore diameter increases the adsorbate molecule encounters a weaker surface attraction such that the enthalpy of interaction approaches the enthalpy of vaporization of the adsorbate.

As mentioned previously, the surface area of a solid is one physical property which is generally reported in the literature for describing the porosity of a material. There have been many advances in the development of theoretical models to aid in the calculation of surface area, but none have reached the point of predicting an adsorption isotherm based on the known properties of the adsorbates and of the adsorbents.[3] One of the earliest models used to describe adsorption, which laid the foundation for many others to follow, was the Langmuir equation (Equation 1-1).[1,3,23] Here P is the equilibrium pressure of A in atmospheres above the solid, SA is the total amount of A adsorbed per gram of solid, n is the number of sites available for adsorption, and K is the equilibrium constant describing the affinity of A for being adsorbed by S. Examination of a plot of P/[SA] vs. P for a homogeneous solid is a straight line of slope $1/n$ and an intercept of $1/n$K. From the determination of n one can use the cross sectional area of the adsorptive to determine the accessible surface area.[3] Likewise, use of the molar volume of the adsorptive with n yields the accessible pore volume.[3]

$$[SA] = \frac{nK[P]}{1 + K[P]} \qquad \text{Equation 1-1}$$

The Langmuir equation describes the adsorption of a molecule based on the assumption that only a monolayer coverage is possible, that there are no adsorbate-adsorbate

interactions, and that the heat of adsorption is independent of surface coverage, meaning that the solid has a homogeneous surface.[1,24] Clearly, it can be inferred from the information provided above, that many, if not all, solids are heterogeneous in nature and are comprised of a distribution of pore sizes and surface defects which exhibit different adsorption potentials.

The BET (Brunauer, Emmett, and Teller) equation (Equation 1-2) was an attempt to improve on the assumptions of Langmuir by including multilayer adsorption.[1,3,25]

$$\frac{X}{n(1-X)} = \frac{1}{Cn_m} + \frac{(C-1)X}{Cn_m} \qquad \text{Equation 1-2}$$

where

$$C = \frac{K_{i,ads}}{K_{j,ads}} \exp \frac{Q_{mono} - Q_{multi}}{RT}$$

Here $X = P/P_o$, and n is the total number of moles of adsorptive adsorbed per gram of solid. The quantities n_m and C are derived from a linear plot of X/n(1-x) vs. X. The BET C constant is a complex quantity with contributions from the equilibrium constants, $K_{i,ads}$ and $K_{j,ads}$, and the enthalpies, Q_{mono} and Q_{multi}, of adsorption for mono- and multilayer formation. The enthalpy of adsorption for the multilayer is generally associated with the enthalpy of vaporization of the adsorptive. The BET equation is generally considered the standard for describing the surface area of solids;[3,26] however, it too has been subjected to criticism due to its limited effective pressure range of 0.05 to 0.3 atmospheres and its

inability to accurately define the surface areas for microporous materials where it may predict too large a surface area.[1,3]

Other adsorption models such as the DR model proposed by Dubinin and Radushkevich[1,27] and the Horvath-Kawazoe[28] model have examined the concept of pore filling in order to establish an understanding of the pore size distribution of solids. Although useful, these models involve extensive mathematical manipulation and the empirical assignment of constants which at times may have to be altered in order to explain or fit the adsorption isotherm. In summarizing the quandary of those interested in understanding adsorption equilibria, Choudhary *et al.* state that no one adsorption model (Langmuir, DR, BET, etc.) was capable of fitting their data for three individual probe gases to the corresponding experimental isotherms for any one of the three zeolites studied.[29] From this statement it is clear that for all of the adsorption models in use, no one particular model has yet to be found applicable for all solids at all pressures for all adsorbates.

Chapter 2 extends a newly reported adsorption model in an attempt to shed new light on the theory of gas-solid equilibria.[30,31] This model is capable of fitting the adsorption data of an experimental isotherm with considerable accuracy. Although similar to the Langmuir equation, the Multiple Equilibria Analysis, MEA, model is designed to treat the adsorption of gaseous molecules as individual adsorption processes and not as site specific interactions as in the Langmuir analysis. The equilibrium constants represent the interactions of adsorbate molecules in pores that are too close in size to be distinguished. As the name suggests, it is believed that multiple adsorption processes

occur in heterogeneous solids and that this model, along with the detailed information that is obtainable, can lead to the prediction of adsorption isotherms for adsorbates not yet tested on a particular solid. Chapter 3 is an extension of the MEA to liquid-solid equilibria where the adsorption of several organic compounds from cyclohexane solutions by silica gel and a carbonaceous adsorbent were studied.

Environmental and safety concerns for the handling and disposal of chemicals and chemical waste has heightened the interest in porous materials serving as adsorbents and catalysts. There are a number of benefits to designing solid acids for use in heterogeneous catalysis. The first is the ease of product separation from the catalyst and the reactants. The second is the ability of some solid acids to be regenerated, thus lowering the amount of acid waste, as well as lowering financial expenditures. Chapter 4 presents the development of a solid acid which is designed to reduce the amount of liquid acids, such as H_2SO_4 and HF, currently in use.

CHAPTER 2
CHARACTERIZATION OF POROUS MATERIALS BY THE MULTIPLE EQUILIBRIA ANALYSIS MODEL

Introduction

The adsorption, whether chemical or physical, of a gas, $A_{(g)}$, by a solid, $S_{(s)}$, can be described by Equation 2-1.

$$S_{(s)} + A_{(g)} \Leftrightarrow SA_{(s)} \qquad \text{Equation 2-1}$$

An equilibrium constant, K, can be written for this physisorption or chemisorption interaction described in Equation 2-1 and rearranged to give Equation 2-2 .[3,24]

$$[SA]_s = \frac{nK[P]}{1+K[P]} \qquad \text{Equation 2-2}$$

Here, n is the capacity for adsorption, $[SA]_s$ is the total amount of A adsorbed per gram of solid, and P is the equilibrium pressure, in atmospheres, of A in equilibrium with the solid. Though Equation 2-2 is similar in form to the Langmuir equation, the derivation with n defined as a process capacity eliminates the assumptions of site specific interactions associated with the Langmuir equation. The key feature of this equation is the treatment of nonspecific adsorption by a distribution type of equilibrium constant that refers to a

process and not to a specific binding site. As a consequence, n refers to a process capacity with the adsorbate undergoing interactions with the solid and neighboring adsorbate molecules.

Porous materials contain a distribution of pore sizes and structural defects which give heterogeneity to the solid.[32] This heterogeneity gives rise to multiple equilibrium expressions which represent the adsorption of a gas in the matrix of a solid. Each of these equilibrium expressions can be described by Equation 2-2. Summation of i expressions like Equation 2-2, to accommodate i multiple adsorption processes, leads to Equation 2-3. The capacities, equilibrium constants, and heats of adsorption define the processes that contribute to the total adsorption isotherm.

$$[SA]_s = \sum_i \frac{n_i K_i [P]}{1 + K_i [P]} \qquad \text{Equation 2-3}$$

Here $[SA]_s$ is the total amount of A adsorbed by the solid, S, in the experiment in moles per gram, n_i, is the capacity for process i in moles, K_i is the equilibrium constant for process i in atm^{-1}, and P is the equilibrium pressure in atmospheres. From Equation 2-2, a plot of $[P]/[SA]_s$ vs. [P] for a one process adsorption isotherm would be linear;[3,24] however, results at low temperatures may cause a curved isotherm, suggesting multiple equilibrium processes.

Analysis of a data set with Equation 2-3 for a three process interpretation involves solving for six unknowns, n_1, n_2, n_3, K_1, K_2, and K_3. The $n_{i,ads}$ values for each process are assumed to be temperature independent; therefore, each new data set, at a different

temperature, introduces only new $K_{i,ads}$ values as unknowns. For a three process analysis, the 6:1 ratio of unknowns to knowns at one temperature becomes 9:2 at two temperatures, and 12:3 at three temperatures. Multiple temperature analyses decrease the ratio of unknown to known parameters which leads to a better definition of the minimum in the fit of the combined data set. In due process, the enthalpies for each adsorption process, $-\Delta H_{i,ads}$, are calculated from the temperature dependent equilibrium constants ($K_{i,ads}$) by plotting ln $K_{i,ads}$ vs. 1/T(K) (van't Hoff plot). Linearity of the graph affords a check on the consistency of the fit parameters for the model employed.

To analyze data, a least squares minimization is used. In order to avoid locking into false minima an estimate of the parameters is required. An isotherm of P/[SA] vs. [P] is segmented into linear regions and a linear regression analysis is performed on the points in each region to obtain preliminary *n* and K values. The slope of a linear portion is equal to 1/*n* and the intercept is equal to 1/*n*K. The number of processes that will be initially employed in the data fit is determined from the minimum number of straight line regions one is able to distinguish in the total isotherm, Figure 2-1. The lowest pressure region is associated with process 1, the next with process 2, continuing until the minimum number of straight line regions is used to fit the entire isotherm. The preliminary *n* and K values obtained for each straight line region are used as starting values in a simplex fitting program designed to fit each of the multiple temperature adsorption data sets for a particular probe simultaneously.

Only one set of *n* values is needed for the fit as the *n*'s are assumed to be temperature independent. Evidence of this temperature independence is apparent in many of the isotherms where the calculated seed values are relatively the same for each

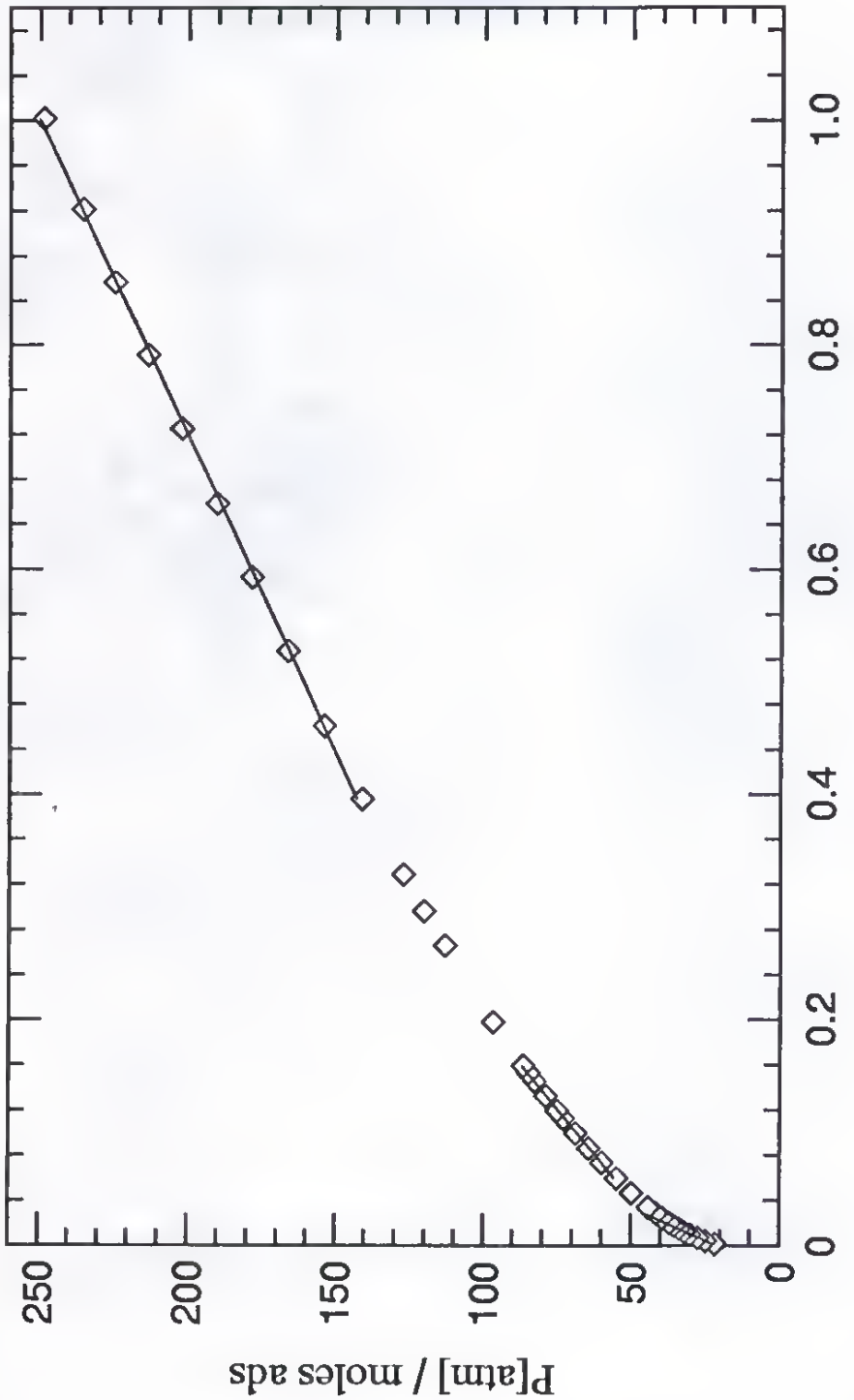

Figure 2-1: Determination of the number of adsorption processes. The lines through the data represent those points selected for a particular process.

corresponding n value at the different temperatures. For a three process fit, the initial value of n_3 is taken from the temperature set closest to the critical temperature of the adsorptive. The value of n_2 is taken from either the same temperature set or the next highest, and n_1 from the highest temperature set. It is at these temperatures that each quantity is the best defined. The initial parameter set then contains one set of n values and a set of K values for each temperature. For the initial fit, each parameter is given a 10% bound and all of the temperature sets are fit simultaneously. After successive fits the bound is reduced to 1% of the parameter. The bound limits the size of the step taken in the search, but not the variation in the final parameter; therefore, the parameters are not sensitive to the bounds selected. The parameters obtained from the initial fit are then entered as the initial parameters for the next fit. The parameters from the second fit are then entered as initial parameters into the third and each successive fit is done accordingly. This procedure is used since several local minima are found during the first few fits. Therefore, the fitting process is not assumed to be complete until all of the parameters cease to vary from fit to fit. To assure oneself that the final minimum reached is not a false minimum, the parameters are changed by several orders of magnitude and the fit is repeated. If the final parameters reach the same values as before, one can feel confident in the data analysis.

Experimental

Adsorption analyses are conducted on a Micromeritics® ASAP 2000 gas analyzer employing chemisorption software. A pressure table consisting of a minimum of 40

pressure points has been selected, Appendix A. The pressure table spans the range from 0.05 to 760 torr, with approximately 50% of the selected pressure points below 350 torr. Pressure tolerances are set for 1% (10 torr pressure transducer) and 1mmHg (100 torr pressure transducer) with a 10 second equilibration time interval between selected pressure points. The data are collected as unsmoothed data and exported to a spreadsheet where the data in pressure (torr) and volume adsorbed (mL g^{-1}) are converted to pressure in atmospheres and moles adsorbed.

Low temperature adsorption experiments (< 25°C) were performed with the aid of liquid N_2 / solvent baths[33] in Dewar flasks supported by the instrument's elevator unit. High temperature adsorption experiments (≥ 25°C) were performed using the heating mantles supplied with the instrument's degas manifold with temperatures maintained to within ± 1°C. Adsorption measurements are typically performed at temperatures above the critical temperature, T_c, of the adsorptive in order to avoid possible condensation of the adsorptive in the pores of the solid.

The gases He and N_2 (99.99% purity) were obtained from Liquid Air, Inc. The gases CH_4, CO, C_2H_6, C_3H_8, and dimethyl ether (DME) (99.99%) were purchased from Matheson Gas Company. The gases SO_2 and SF_6 were purchased from Aldrich Chemical in lecture bottle form. Properties of the selected gases are summarized in Table 2-1. Sample preparation consisted of drying the adsorbent on the instrument's degas manifold at elevated temperature and reduced pressure (<10^{-3} torr) for a minimum of 8 hours. Typical sample weights were on the order of 0.25 to 0.3 g.

Carbon, hydrogen, and nitrogen analyses (C,H,N) were performed by the University of Florida elemental analysis laboratory. The results are listed in Table 2-2. For comparative purposes, surface area and pore volume data were obtained from the N_2 isotherm at 77K using a Micromeretics® ASAP 2000 instrument. Surface areas were determined using a five point BET calculation.[1,3,25] Micropore volume was determined using the Harkins-Jura t-plot model with thickness parameters from 5.5-9.0 Å.[34] The BJH desorption curve was used for calculating meso- and macropore volumes.[35] Table 2-2 lists the parameters found from N_2 porosimetry for the various adsorbents.

Results and Discussion

Chemically different porous carbonaceous and silca based metal-oxide adsorbents were studied with a series of probe gases. Ambersorb®572 (A-572, lot #2201) is a predominantly carbon containing pyrolized polymeric adsorbent, and PPAN (PLR 0246), a pyrolyzed poly-acrylonitrile adsorbent. Both solids were supplied by the Rohm and Haas Company. The metal oxide adsorbents consisted of a commercial silica gel (Fisher SG, lot# 934403) and a commercial sample of the zeolite HZSM-5 (Si/Al = 50, PQ Corporation). The gases used were selected to encompass a range of polarity, polarizability, and donor-acceptor properties. Helium was used as a reference zero point to determine the dead volume of the solids. The physical properties of the selected adsorptives are listed in Table 2-1.

Results from the fitting of the multiple temperature data indicate that for a solid where three processes are believed to be occurring, the use of temperatures above the critical temperature provide useful information for the first two processes. At higher

Table 2-1: Summary of Gases and Physical Properties[36]

Probe Gas	MW g/mole	Polarizability[a] Å^3	Dipole Moment Debye[b]	Molar Volume[c] mL/mol	Critical Temperature °C	Normal Boiling Point °C	ΔH_v kcal/mol	van der Waals Const. [a]	Cross Sectional Area [Å^2]	Kinetic Diameter[d] Å
N_2	28.01	1.74	0	35.4	146.9	-195.8	1.33	1.390	16.2	3.64
CO	28.01	1.95	0.13	34.9	140.2	-191.5	1.44	1.485	15.0	3.76
CH_4	16.04	2.59	0	37.8	-82.60	-161.5	1.95	2.253	17.8	3.8
C_2H_6	30.07	4.47	0	52.6	32.3	-88.65	3.52	5.489	23.0	~4.3
C_3H_8	44.10	6.29	0.084	75.0	96.7	-42.1	4.49	8.664	36.1	4.3
DME	46.07	5.16	1.3		127	-25	36.78	8.073		
SF_6	146.05	6.54	0	75.5	45.55	-63.8_{sub}	4.08		26.7	5.5
SO_2	64.06	4.28	1.63	43.8	157.5	-10.0	5.96	6.714	27.1	3.6

Table 2-2: Physical Properties of Adsorbents

	Fisher SG	HZSM-5	A572	PPAN
BET Surface Area $[m^2g^{-1}]^a$	508	402	1222.7	873.7
Pore Volume [mL g^{-1}]				
Micropore[b]	0.02	0.15	0.45	0.33
Mesopore[c]	0.33	0.17	0.35	0.19
Macropore[c]	-----	-----	0.20	0.10
CHN Analysis				
%C	0	0.61	91.3	70.18
%H	0.78	0.43	0.33	1.66
%N	0	0.25	0	5.31

a. Surface area and pore volume data are obtained from N_2 porosimetry at 77K.

b. Micropore volumes calculated from the Harkins-Jura t-plot model.

c. Meso- and Macropore volumes calculated from Barrett-Joyner-Halenda (BJH) desorption data.

temperatures less adsorptive is taken up and the complete adsorption process spans a larger range of pressures before they are complete. Process 3 is incomplete under conditions where Process 1 and Process 2 are well defined. Since more adsorptive is taken up as the temperature decreases, Figure 2-2, Process 1 determination will have a large error as it may reach capacity in the first two or three pressure points. However, at this temperature more of the data points have significant contributions from Process 3. Therefore, Process 3 is best defined by low temperature data near the critical temperature of the adsorbate. Process 1 is best defined at higher temperatures. Resolution of Process 2 appears to be good at all temperatures. Determination of the process parameters is not considered to be adequate until the final process capacity is at least 70 % of the total amount adsorbed at the lowest temperature.

Carbonaceous Adsorbents: A-572 and PPAN

The amorphous, carbonaceous adsorbents A-572 and PPAN were examined for their abiltiy to adsorb various probe molecules. Table 2-3 summarizes the results of the data fits for the adsorbents where n_i is the capacity of the solid for the i^{th} adsorption process in millimoles per gram of solid and $K_{i,ads}$, the adsorption equilibrium constant in atm^{-1}, is a measure of the affinity of the probe to be adsorbed by the solid. The optimized *n* and K values reported in Table 2-3 can be used in Equation 2-3 to solve for $[SA]_s$ for each process. Figure 2-3 shows the process resolved isotherms for CH_4 adsorption by A-572. The resolved isotherms illustrate the capacities for the individual processes and the pressures at which maximum capacity for a process is reached. The initial slope of the

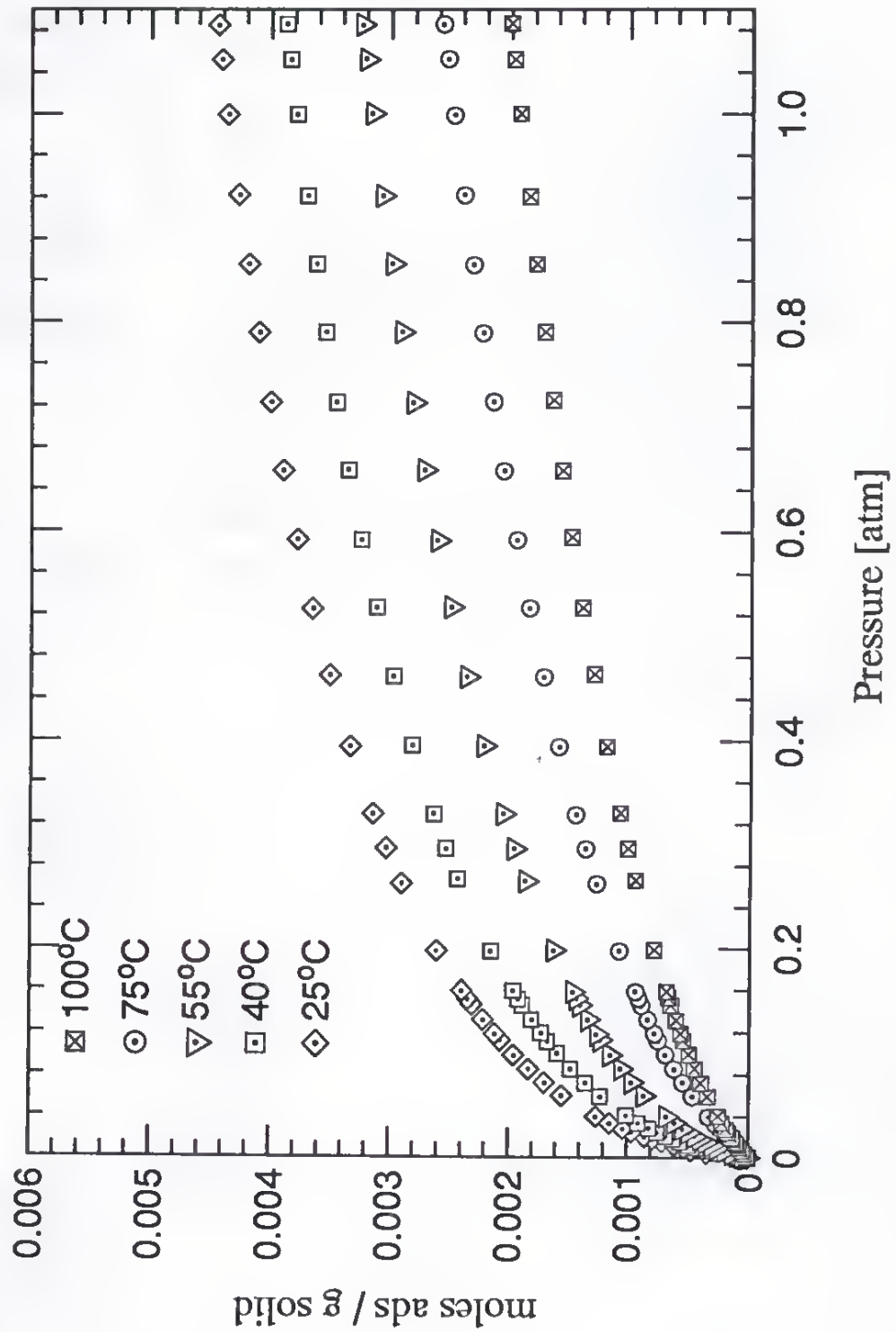

Figure 2-2: Effect of Temperature on the Amount of Adsorbate Adsorbed.

Table 2-3: Equilibrium Constants, *n*-values, Enthalpies, and Free Energies

N_2 / A572						
$n_1 = 0.463 \pm 0.006$			$n_2 = 1.79 \pm 0.04$		$n_3 = 5.3 \pm 0.2$	
$-\Delta H_1 = 4.80 \pm 0.01$			$-\Delta H_2 = 4.3 \pm 0.2$		$-\Delta H_3 = 3.0 \pm 0.2$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
-93	88.15±0.02	1.6022	8.626±0.005	0.7708	0.752±0.001	-0.102
-43	4.5±0.1	0.69	0.72±0.03	-0.15	0.111±0.009	-1.004
0	0.922±0.002	-0.0441	0.1379±0.001	-1.0747	0.046±0.0002	-1.674
N_2 / PPAN						
$n_1 = 0.50 \pm 0.01$			$n_2 = 1.59 \pm 0.09$		$n_3 = 3.6 \pm 0.2$	
$-\Delta H_1 = 4.8 \pm 0.1$			$-\Delta H_2 = 4.4 \pm 0.3$		$-\Delta H_3 = 2.70 \pm 0.1$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
-93	84.65±0.02	1.5877	8.723±0.007	0.7748	0.813±0.003	-0.0739
-43	4.21±0.08	0.657	0.66±0.03	-0.19	0.12±0.01	-0.98
25	0.46±0.01	-0.46	0.043±0.004	-1.86	0.042±0.002	-1.87
CO / A572						
$n_1 = 0.52 \pm 0.01$			$n_2 = 1.90 \pm 0.09$		$n_3 = 4.9 \pm 0.9$	
$-\Delta H_1 = 5.3 \pm 0.3$			$-\Delta H_2 = 4.3 \pm 0.3$		$-\Delta H_3 = 3.4 \pm 0.2$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
-93	249±2	1.9740	19.8±0.5	1.0690	1.4±0.2	0.110
-77	60±2	1.60	5.8±0.4	0.69	0.5±0.2	-0.200
-62	26.4±0.6	1.372	3.1±0.2	0.4800	0.34±0.06	-0.460
-43	9.7±0.61	1.03	1.37±0.03	0.1450	0.16±0.01	-0.820
CO / PPAN						
$n_1 = 0.52 \pm 0.01$			$n_2 = 1.90 \pm 0.09$		$n_3 = 4.9 \pm 0.9$	
$-\Delta H_1 = 5.3 \pm 0.3$			$-\Delta H_2 = 4.3 \pm 0.3$		$-\Delta H_3 = 3.4 \pm 0.2$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
-93	243±1	1.965	18.7±0.5	1.048	1.3±0.2	0.10
-43	8.8±0.3	0.99	1.10±0.08	0.0452	0.15±0.04	-0.88
25	0.70±0.03	-0.21	0.05±0.01	-1.8	0.050±0.005	-1.78
n_i in mmoles, K_i in atm^{-1}, $-\Delta H_i$ in kcal $mole^{-1}$						

Table 2-3 continued

CH_4 / A572						
$n_1 = 0.94\pm0.01$			$n_2 = 2.5\pm0.1$		$n_3 = 5\pm1$	
$-\Delta H_1 = 6.2\pm0.4$			$-\Delta H_2 = 5.1\pm0.2$		$-\Delta H_3 = 4.0\pm0.3$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
-77	359.6±0.6	2.2922	20.1±0.2	1.168	1.8±0. 1	0.22
-62	100±2	1.93	7.9±0.6	0.87	0.8±0.3	-0.07
-43	23.7±0. 2	1.447	2.41±0.07	0.402	0.30±0.03	-0.55
0	4.10±0.01	0.766	0.505±0.004	-0.370	0.103±0.002	-1.235
CH_4 / PPAN						
$n_1 = 0.29\pm0.01$			$n_2 = 1.40\pm0.05$		$n_3 = 3.6\pm0.2$	
$-\Delta H_1 = 6.81\pm0.06$			$-\Delta H_2 = 5.59\pm0.01$		$-\Delta H_3 = 4.70\pm0.03$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
-43	91.2±0.1	2.063	9.98±0.02	1.051	0.933±0.007	-0.0316
0	8.6±0.1	1.17	1.46±0.02	0.204	0.186±0.009	-0.912
25	2.9±0.1	0.64	0.60±0.03	-0.30	0.09±0.01	-1.5
40	1.93±0.08	0.409	0.39±0.02	-0.58	0.061±0.007	-1.74
C_3H_8 / A572						
$n_1 = 0.198\pm0.003$			$n_2 = 1.01\pm0.01$		$n_3 = 2.5\pm0.1$	
$-\Delta H_1 = 12\pm3$			$-\Delta H_2 = 9.4\pm0.3$		$-\Delta H_3 = 8.3\pm0.6$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
125	118.8±0.7	3.7787	13.4±0.1	2.050	1.20±0.05	0.145
150	29.5±0.4	2.844	6.80±0.07	1.611	0.68±0.03	-0.32
175	23.3±0.2	2.802	3.52±0.05	1.120	0.37±0.02	-0.90
C_3H_8 / PPAN						
$n_1 = 0.221\pm0.004$			$n_2 = 0.87\pm0.02$		$n_3 = 1.5\pm0.1$	
$-\Delta H_1 = 12.6\pm0.3$			$-\Delta H_2 = 9\pm1$		$-\Delta H_3 = 8\pm2$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
125	86.1±0.7	3.524	9.4±0.2	1.77	1.2±0.1	0.15
150	33.0±0.2	2.940	5.26±0.06	1.396	0.74±0.04	-0.25
175	15.0±0.3	2.411	2.50±0.07	0.815	0.34±0.04	-0.97
n_i in mmoles, K_i in atm^{-1}, $-\Delta H_i$ in kcal $mole^{-1}$						

Table 2-3 continued

C_2H_6 / A572						
$n_1 = 0.318\pm0.005$			$n_2 = 1.42\pm0.03$		$n_3 = 3.7\pm0.3$	
$-\Delta H_1 = 10.2\pm0.4$			$-\Delta H_2 = 8.1\pm0.2$		$-\Delta H_3 = 6.8\pm0.2$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
40	176.7±0.6	3.2186	15.0±0.1	1.683	1.35±0.05	0.185
55	74±1	2.81	7.6±0.2	1.33	0.75±0.08	-0.19
70	42.0±0.4	2.548	4.81±0.09	1.072	0.53±0.03	-0.43
100	13.9±0.3	1.949	1.88±0.07	0.466	0.23±0.03	-1.08
SO_2 / A572						
$n_1 = 0.9322\pm0.0005$			$n_2 = 4.7\pm0.1$		$n_3 = 6\pm2$	
$-\Delta H_1 = 9.4\pm0.2$			$-\Delta H_2 = 8.1\pm0.1$		$-\Delta H_3 = 8.0\pm0.1$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
25	360±560	3.5	11.8±0.3	1.463	2.8±0.2	0.61
40	140±35	3.06	6.1±0.9	1.13	1.4±0.9	0.22
55	66±15	2.7	3.4±0.8	0.80	0.8±0.6	-0.1
75	30±4	2.35	1.6±0.5	0.32	0.4±0.4	-0.6
SO_2 / PPAN						
$n_1 = 0.658\pm0.00002$			$n_2 = 0.69\pm0.002$		$n_3 = 4.01\pm0.2$	
$-\Delta H_1 = 7.1\pm2.4$			$-\Delta H_2 = 1.1\pm0.1$		$-\Delta H_3 = 4.8\pm0.4$	
T°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$	K_3	$-\Delta G_3$
25	2E6±1E6	5.9	209±60	3.2	14.2±0.3	1.6
40	2E3±4E4	4.8	82.6±20	2.7	6.7±0.4	1.2
55	900±8600	4.4	36.2±5.5	2.3	3.4±0.1	0.8
75	300±800	3.9	14.0±2.3	1.8	1.5±0.9	0.3
n_i in mmoles, K_i in atm^{-1}, $-\Delta H_i$ in kcal $mole^{-1}$						

resolved processes provides some indication as to the affinity for adsorption in that process.

The equilibrium constants are temperature dependent and are a factor of the inherent physical properties (polarizability, van der Waals, etc.) of the adsorbent and adsorptive. For small pores, the equilibrium constant will be greater than that

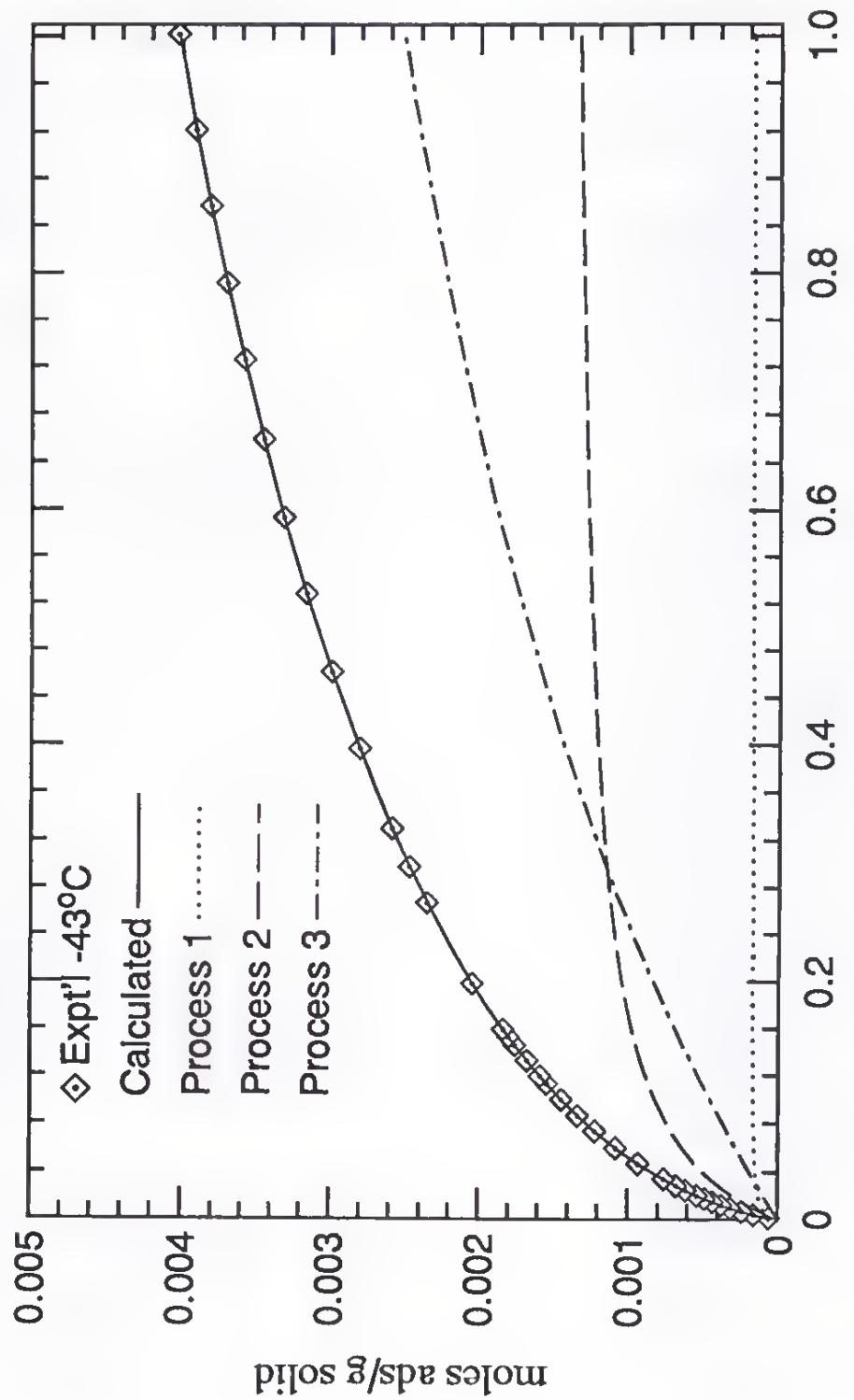

Figure 2-3: Process Resolved Isotherms for CH_4 Adsorption by A-572.

observed for larger pores due to greater interaction of the adsorbate with the walls of the solid (see Chapter 1, Figure 1-2). Larger pores allow more freedom within the pore structure such that an adsorbate molecule moves from one wall to another. Figure 2-4 shows the ln $K_{1,ads}$ vs. 1/T(K) plots for the adsorbates studied with A-572. The creditability of the model can be appreciated in the linearity of these adsorbates and the calculated enthalpies whose values are indicative of physisorption processes.[18]

An interesting trend is observed among the solids studied. As the van der Waals [*a*] parameter of the adsorbates increases so do the equilibrium constants for adsorption. The van der Waals attraction parameter [*a*] is a measure of the strength of interaction of like molecules for one another. The square root of [*a*] should characterize the relative attraction of gas molecules for the solid surface. A plot of ln $K_{1,ads}$ or $-\Delta H_{1,ads}$ vs. vdW $[a]^{1/2}$ for A-572 is linear for the probes examined, Figure 2-5. This not only provides support for the meaning of the fit parameters in the context of the model used, but also permits one to obtain an estimate of the equilibrium constant or enthalpy for the adsorption of molecules not yet studied. This can be of practical utility when one is selecting adsorbents for specific adsorption applications. Deviations from linearity will indicate contributions other than nonspecific interactions present in the adsorption process. A least squares analysis of such plots yields a coefficient which is representative of the overall surface attraction for a particular process. With the exception of SO_2 on PPAN, all of the adsorbates studied fall on or near the best fit lines given in Equations 2-4 through 2-8.

A-572

$$-\Delta H_1 = 3.0\ (\pm 0.3)\ a^{1/2} + 1.54\ (\pm 0.53) \qquad R^2 = 0.96 \qquad \text{Equation 2-4}$$

$$-\Delta H_2 = 2.7\ (\pm 0.1)\ a^{1/2} + 1.31\ (\pm 0.29) \qquad R^2 = 0.98 \qquad \text{Equation 2-5}$$

$$-\Delta H_3 = 3.24\ (\pm 0.15)\ a^{1/2} - 0.75\ (\pm 0.31) \qquad R^2 = 0.98 \qquad \text{Equation 2-6}$$

PPAN

$$-\Delta H_1 = 3.32\ (\pm 0.33)\ a^{1/2} + 1.16\ (\pm 0.61) \qquad R^2 = 0.98 \qquad \text{Equation 2-7}$$

$$-\Delta H_2 = 2.96\ (\pm 0.57)\ a^{1/2} + 0.58\ (\pm 1.10) \qquad R^2 = 0.93 \qquad \text{Equation 2-8}$$

Within the calculated error of the coefficients, the values exhibit a relatively uniform surface attraction for the individual processes for A-572 and PPAN, indicating that the magnitude of the equilibrium constants is determined by the overall size of the pore in relation to the adsorbate. Specific donor-acceptor interactions of adsorbate molecules with a solid surface are expected to give rise to deviations in the van der Waals plots if these interactions are stronger than those in the gaseous adsorbate. Therefore, we conclude that the solid-adsorbate interactions for the systems described in the above equations represent nonspecific interactions for those pores which are on the order of molecular dimensions for the adsorbates studied.

It is significant that the enthalpies for N_2, CO, CH_4, C_2H_6, and C_3H_8 fall on a straight line for Process 1 even though our analysis of the capacities indicated that a different distribution of micropores is utilized for the different gases. Thus, Process 1 utilizes pore widths of molecular dimensions. Process 2 involves dimensions up to two

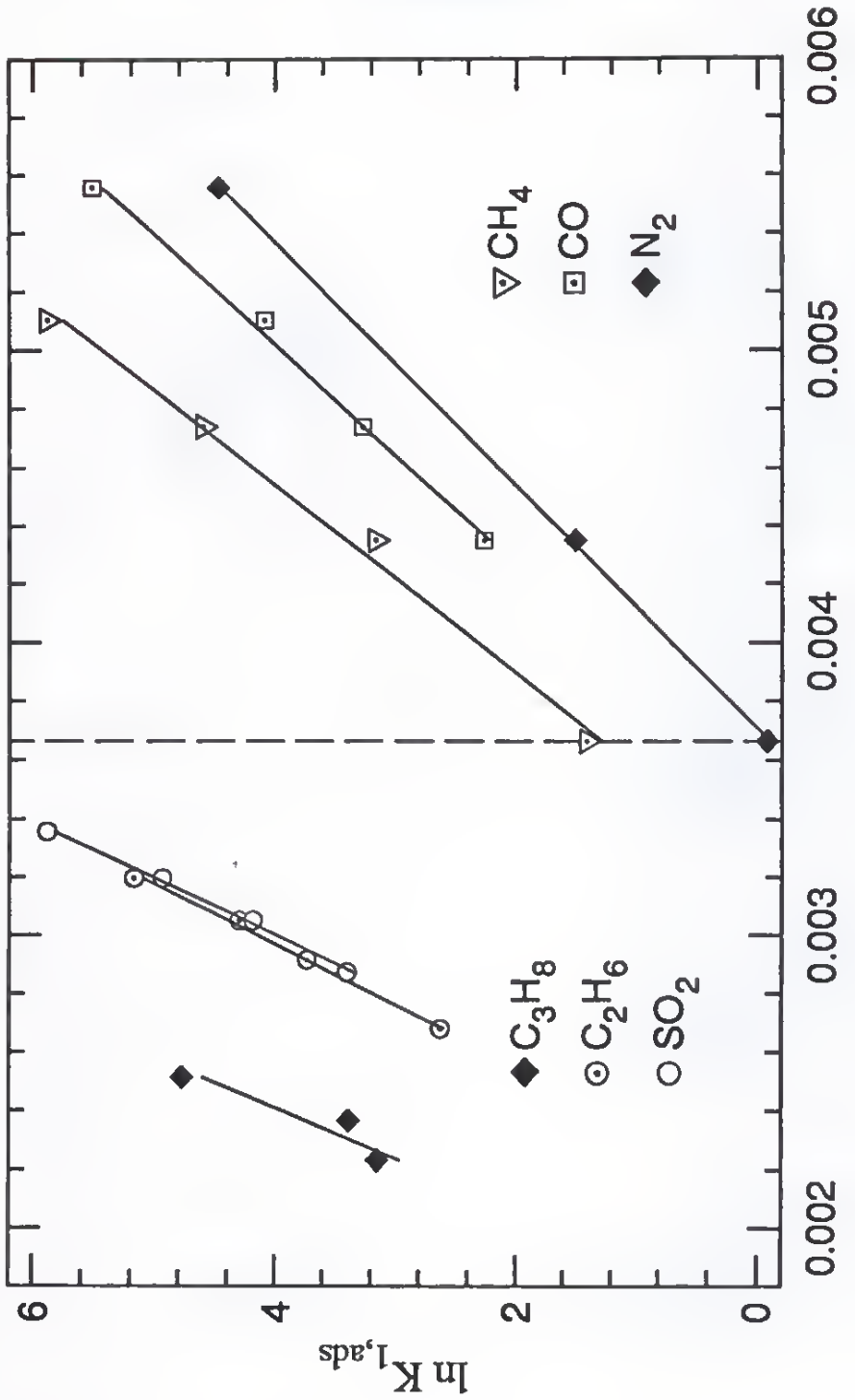

Figure 2-4: ln K vs. 1/T(K) Plot for the Gaseous Probes Adsorbed by A-572.

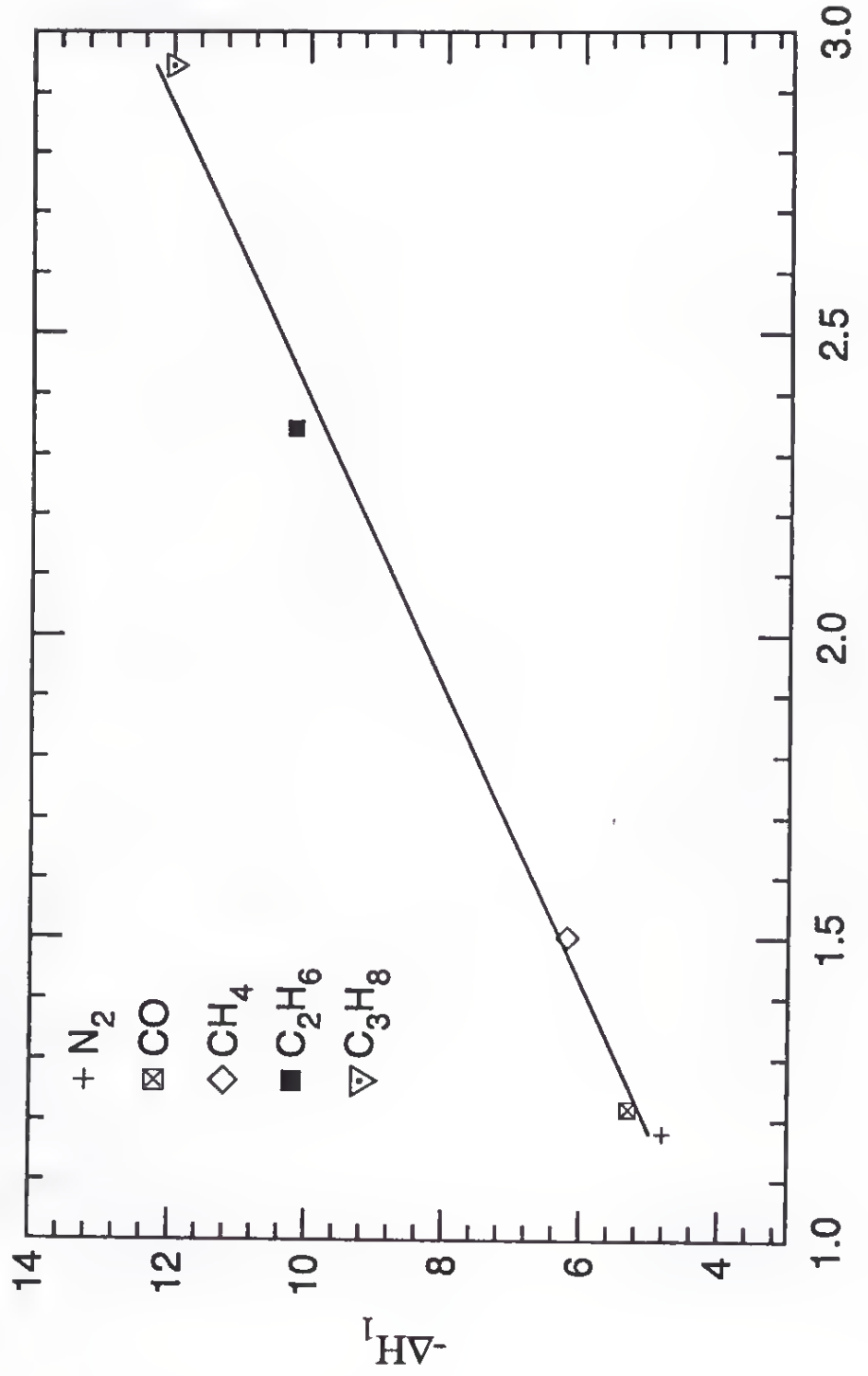

Figure 2-5: $-\Delta H_1$ vs. Square Root of van der Waals [a] for A-572.

molecules at their van der Waals separation interacting with the walls and each other. Process 3 involves larger pores in which molecules interact strongly with one wall and weakly or not at all with the opposite wall. In this manner, a given process i is fundementally the same for all probes studied, but different dimension pores are utilized for the ith process of each probe.[37]

The relative importance of dispersion and nonspecific dipole-dipole interaction can be inferred from plots of ln $K_{i,ads}$ or $-\Delta H_{i,ads}$ versus polarizability (α) of the adsorbate. Comparisons of these plots for different adsorbates describe the relative effective surface polarizability of the solid. Equations 2-9 through 2-13 represent the equations for the best fit lines for N_2, CO, CH_4, C_2H_6, and C_3H_8 for A-572 and PPAN. Note that the coefficients again are within experimental error for each of the processes listed indicating a uniform surface polarization.

A-572

$-\Delta H_1 = 1.19\ (\pm 0.7)\ \alpha + 3.00\ (\pm 0.6)$ $\quad R^2 = 0.94$ Equation 2-9

$-\Delta H_2 = 1.07\ (\pm 0.9)\ \alpha + 2.58\ (\pm 0.3)$ $\quad R^2 = 0.98$ Equation 2-10

$-\Delta H_3 = 1.25\ (\pm 0.07)\ \alpha + 0.90\ (\pm 0.3)$ $\quad R^2 = 0.99$ Equation 2-11

PPAN

$-\Delta H_1 = 1.30\ (\pm 0.12)\ \alpha + 2.71\ (\pm 0.4)$ $\quad R^2 = 0.98$ Equation 2-12

$-\Delta H_2 = 1.15\ (\pm 0.24)\ \alpha + 2.02\ (\pm 0.9)$ $\quad R^2 = 0.92$ Equation 2-13

The *n* values determined on most gas-solid equilibria studied to date indicate that the three processes are occurring in the micropores of these solids. Information similar to

that presented in Table 2-3 can be used to estimate the accessible micropore surface area of the solid based upon the cross sectional area[38] or kinetic diameter[13] of the adsorptive. Pore volumes for the individual processes can be determined from the molar volume of the adsorptive. The adsorptives studied vary in size such that the pores for Process 1 of one adsorptive will not be the same for a larger adsorptive. Therefore, the process capacities of the MEA model are relevant to the micropore distribution of porous materials that are characteristic of the specific adsorptive. Table 2-4 lists the surface areas and volume capacities for the processes of A-572 and PPAN. The MEA surface areas are considerably lower than the reported BET surface area of ~1200 $m^2 g^{-1}$. This is believed to be a result of condensation of N_2 at 77K in the larger pores of the solids. This also would allow for the pore volumes calculated by MEA to be much smaller than that determined from standard nitrogen porosimetry.

Silica Gel and Zeolites

Silica gel (amorphous) and HZSM-5 (crystalline) afford samples of similar composition and vastly different porosity that can be compared to the amorphous carbons. Silica gel consists mainly of mesopores, while N_2 porosimetry suggests that HZSM-5 contains both micro- and mesopores, Table 2-2. X-ray data indicate that HZSM-5 is a microporous material contradicting N_2 porosimetry results. Nonpolar adsorbates of varying dimensions and shapes were selected to investigate the potential of the MEA model in discerning porosity differences.

Table 2-4: Process Resolved Pore Volumes and Surface Areas for A572 and PPAN

	A572			PPAN		
	N_2			N_2		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	0.463	0.016	45	0.499	0.018	49
2	1.790	0.063	175	1.588	0.056	155
3	5.335	0.189	520	3.585	0.127	350
Total	7.588	0.269	740	5.672	0.201	553
	CO			CO		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	0.520	0.018	47	0.570	0.020	51
2	1.898	0.066	171	1.802	0.063	163
3	4.932	0.172	445	3.642	0.127	329
Total	7.351	0.257	664	3.014	0.210	543
	CH_4			CH_4		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	0.938	0.035	100	0.285	0.011	31
2	2.492	0.094	267	1.401	0.053	150
3	5.394	0.204	578	3.628	0.137	389
Total	8.824	0.334	945	5.314	0.201	569
	C_3H_8			C_3H_8		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	0.198	0.015	43	0.221	0.017	48
2	1.007	0.075	219	0.874	0.066	190
3	2.488	0.187	541	1.529	0.115	332
Total	3.693	0.277	803	2.624	0.197	570
	C_2H_6					
Process	mmol ads	ml ads	area[m^2g^{-1}]			
1	0.318	0.017	44			
2	1.422	0.075	197			
3	3.718	0.196	515			
Total	5.459	0.287	756			

Adsorption Isotherms

For HZSM-5, and related solids with the MFI structure,[39] the straight (elliptical shaped, 5.4 x 5.6 Å) and zig-zag (almost circular shaped, 5.1 x 5.4 Å) channels differ slightly in dimension, so at least two processes are expected.[40] The calculated $n_{i,ads}$ values and the temperature dependent $K_{i,ads}$ values for all systems studied are listed in Table 2-5. The symbols in Figure 2-6 and Figure 2-7 show representative adsorption isotherms for HZSM-5 (Si / Al = 50) at two of the several temperatures required for a MEA analysis.

The temperature dependence of $K_{1,ads}$ and $K_{2,ads}$ gives the enthalpies ($-\Delta H_{i,ads}$) and entropies ($-\Delta S_{i,ads}$) for the processes via the van't Hoff equation ($\ln K_i = -\Delta H_i / RT + \Delta S_i / R$):

N_2 $\ln K_1 = 2468.89(1/T) - 10.4877$; $\ln K_2 = 1557.767(1/T) - 7.99366$

CO $\ln K_1 = 3072.531(1/T) - 11.0588$; $\ln K_2 = 2606.553(1/T) - 11.0546$

$\ln K_3 = 1553.595(1/T) - 7.8888$

CH_4 $\ln K_1 = 2585.9(1/T) - 9.19493$; $\ln K_2 = 2286.986(1/T) - 10.4992$

C_2H_6 $\ln K_1 = 4275.89(1/T) - 11.4402$; $\ln K_2 = 4643.942(1/T) - 17.5608$

C_3H_8 $\ln K_1 = 4856.225(1/T) - 10.3288$; $\ln K_2 = 6234.666(1/T) - 15.7839$

SF_6 $\ln K_1 = 3819.4(1/T) - 8.30587$; $\ln K_2 = 4803.92(1/T) - 13.7946$

DME $\ln K_1 = 11247.42(1/T) - 17.4082$; $\ln K_2 = 6523.715(1/T) - 11.8505$;

$\ln K_3 = 5320(1/T) - 12.2464$

These results are summarized in Table 2-6 and the ln $K_{1,ads}$ vs. 1/T(K) plots for HZSM-5 are shown in Figure 2-8. The linearity of these plots, and enthalpies, with magnitudes expected for physisorption processes, indicate that meaningful parameters result from the model.

In our examination of the carbonaceous adsorbents mentioned in the previous section, the most exothermic process, Process 1 was assigned to adsorption in the smallest channels/pores of the solid, and Process 2 to the larger channels/pores. Comparison of the kinetic diameters of the probes (Table 2-1) with the average channel diameter of 5.5 Å for HZSM-5 indicates that the channel is ~1.0 to 1.5 times as large as the kinetic diameter of the gas molecules studied. Thus, in contrast to carbon where the adsorbate selects those pores of comparable dimensions for Process 1 from the distribution of pore sizes available, Process 1 in zeolites corresponds to different adsorbate-wall interactions for the different size adsorbate. For HZSM-5, and similar zeolites, the channels of the solid approximate cylinders. For small molecules, *i.e.* N_2, adsorbate-adsorbent interactions will occur with one side of the channel. Based on the kinetic diameter of N_2, and the diameter of the channel, two molecules cannot occupy opposite positions on adjacent walls. A single N_2 molecule is expected to adsorb on the channel surface providing the maximum surface interaction and will interact weakly with the rest of the cylinder wall. As the adsorbates increase in size, interaction with the distant walls of the channel increases becoming a maximum when the molecular diameter is that of the cylinder. Thus, the increasing values of the enthalpies for Process 1 (Table 2-5) as the size of the adsorbate increases is due to

Table 2-5: Equilibrium Constants, *n*-values, Enthalpies, Free Energies

N_2 / HZSM-5				
$n_1 = 1.5\pm0.01$			$n_2 = 1.3\pm0.01$	
$-\Delta H_1 = 4.9\pm0.3$			$-\Delta H_2 = 3.1\pm0.4$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
-93	22.7±0.8	1.116	2.3±0.3	0.292
-43	1.5±0.01	0.188	0.2±0.01	-0.704
0	0.3±0.01	-0.731	0.8±0.01	-1.344
25	0.09±0.04	-1.423	0.09±0.05	-1.445

CO / HZSM-5				
$n_1 = 0.6089\pm0.0001$		$n_2 = 1.222\pm0.005$		$n_3 = 1.7\pm0.4$
$-\Delta H_1 = 6.1\pm0.08$		$-\Delta H_2 = 5.2\pm0.3$		$-\Delta H_3 = 3.1\pm0.5$
Temp°C	K_1		K_2	K_3
-93	417±9		28±4	2±5
-43	8.7±0.6		1.5±0.3	0.2±0.3
-16	2.56±0.07		0.46±0.03	0.15±0.04
0	1.234±0.004		0.178±0.002	0.151±0.002

CH_4 / HZSM-5				
$n_1 = 0.2\pm0.01$			$n_2 = 0.92\pm0.06$	
$-\Delta H_1 = 5.1\pm0.03$			$-\Delta H_2 = 4.5\pm0.1$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
-84	86±17	1.672	5±7	0.605
-42	8.14±0.07	0.962	0.55±0.07	-0.276
-16	2.31±0.01	0.427	0.2±0.02	-0.846
0	1.28±0.01	0.133	0.13±0.03	-1.123

C_3H_8 / HZSM-5				
$n_1 = 0.8189\pm0.0007$			$n_2 = 0.85\pm0.03$	
$-\Delta H_1 = 9.7\pm0.5$			$-\Delta H_2 = 12.4\pm0.9$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
75	38±4	2.515	7.9±2.1	1.429
125	5.98±0.9	1.414	0.9±0.8	-0.083
150	3.58±0.12	1.072	0.44±0.09	-0.7308
175	1.58±0.05	0.407	0.13±0.04	-1.816

n_i in mmoles, K_i in atm^{-1}, $-\Delta H_i$ in kcal $mole^{-1}$

Table 2-5 continued

C_2H_6 / HZSM-5				
n_1 =1.92±0.06			n_2 =0.6±5	
$-\Delta H_1$ = 8.5±0.2			$-\Delta H_2$ = 9.2±1.7	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
-16	189±10	2.676	2±32	0.354
0	68±2	2.288	0.7±7	-0.193
25	17.6±0.2	1.698	0.2±0.6	-0.953
40	9.41±0.02	1.394	0.04±0.08	-2.002
50	5.28±0.02	1.068	0.02±0.09	-2.511
75	2.61±0.01	0.663	0.03±0.05	-2.425
SF_6 / HZSM-5				
n_1 = 0.56±0.005			n_2 =1.2±0.1	
$-\Delta H_1$ = 7.6±0.3			$-\Delta H_2$ = 9.5±0.006	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
50	34.1±0. 2	2.265	2.94±0.09	0.683
65	19.6±0.2	1.998	1.5±0.1	0.2723
80	12.57±0.06	1.777	0.83±0.03	-0.156
ZSM-5 / DME				
n_1 = 0.616±0.05		n_2 = 0.15±3	n_3 = 1±55	
$-\Delta H_1$ = 22.4±4.5		$-\Delta H_2$ = 13±0.7	$-\Delta H_1$ = 10.6±1.3	
Temp°C	K_1	K_2	K_3	
150	8324±6	35±26	1±3	
175	3056±3	16±13	0.7±1	
200	492±5	7±191	0.3±25	
n_i in mmoles, K_i in atm^{-1}, $-\Delta H_i$ in kcal $mole^{-1}$				

the increased polarizabilities of the larger molecules, and also to increased interaction of the adsorbate with the surrounding walls.

With the carbonaceous adsorbents, the term process has been used to describe collectively the affinity ($K_{i,ads}$) and the strength ($-\Delta H_{i,ads}$) of adsorption of a gas molecule into a particualr size pore distribution. Process 1 would correspond to pores that were on the order of the size of the gas molecule which in turn had the greatest enthalpy of

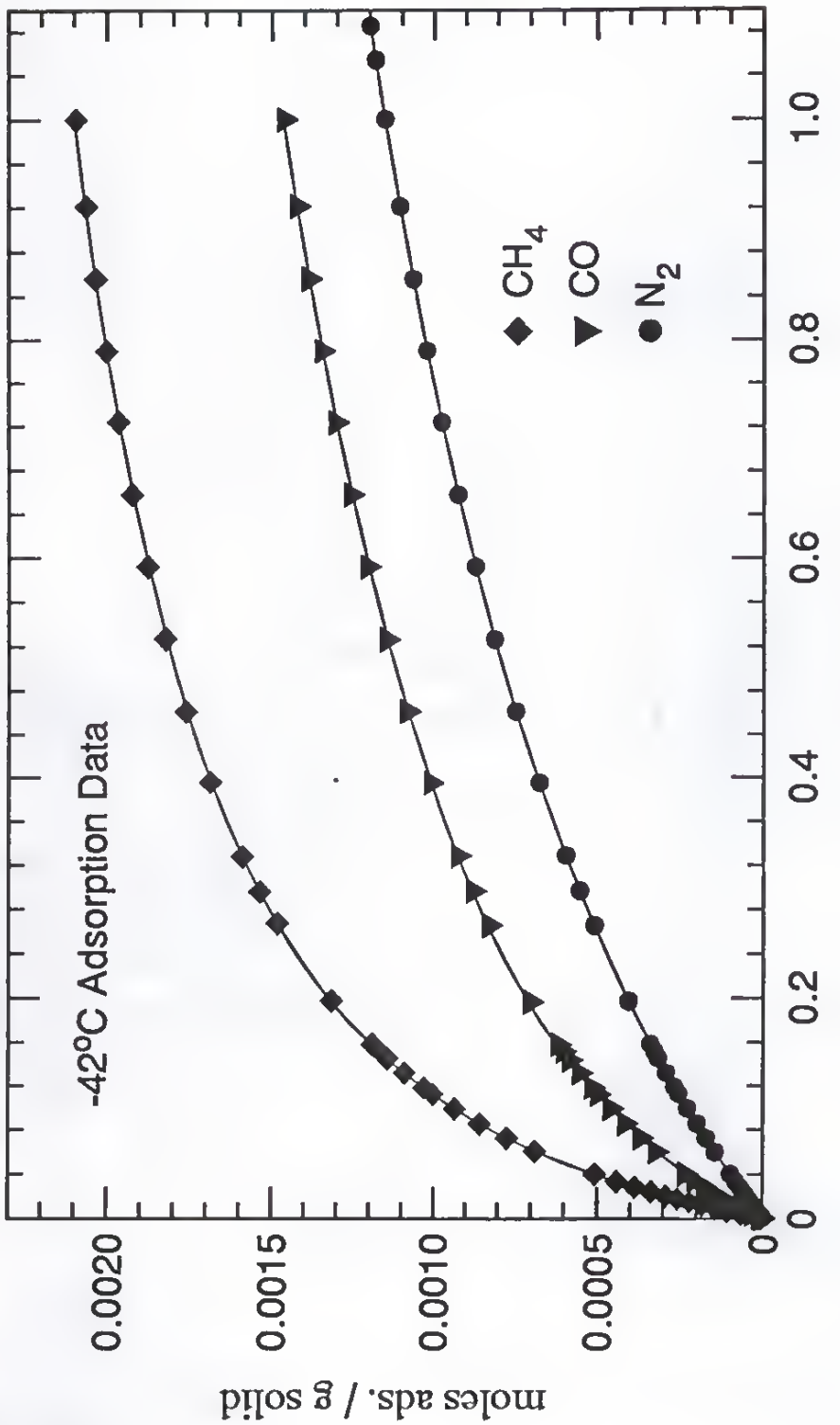

Figure 2-6: Adsorption Isotherms for the Non-Condensible Gases Studied with HZSM-5.

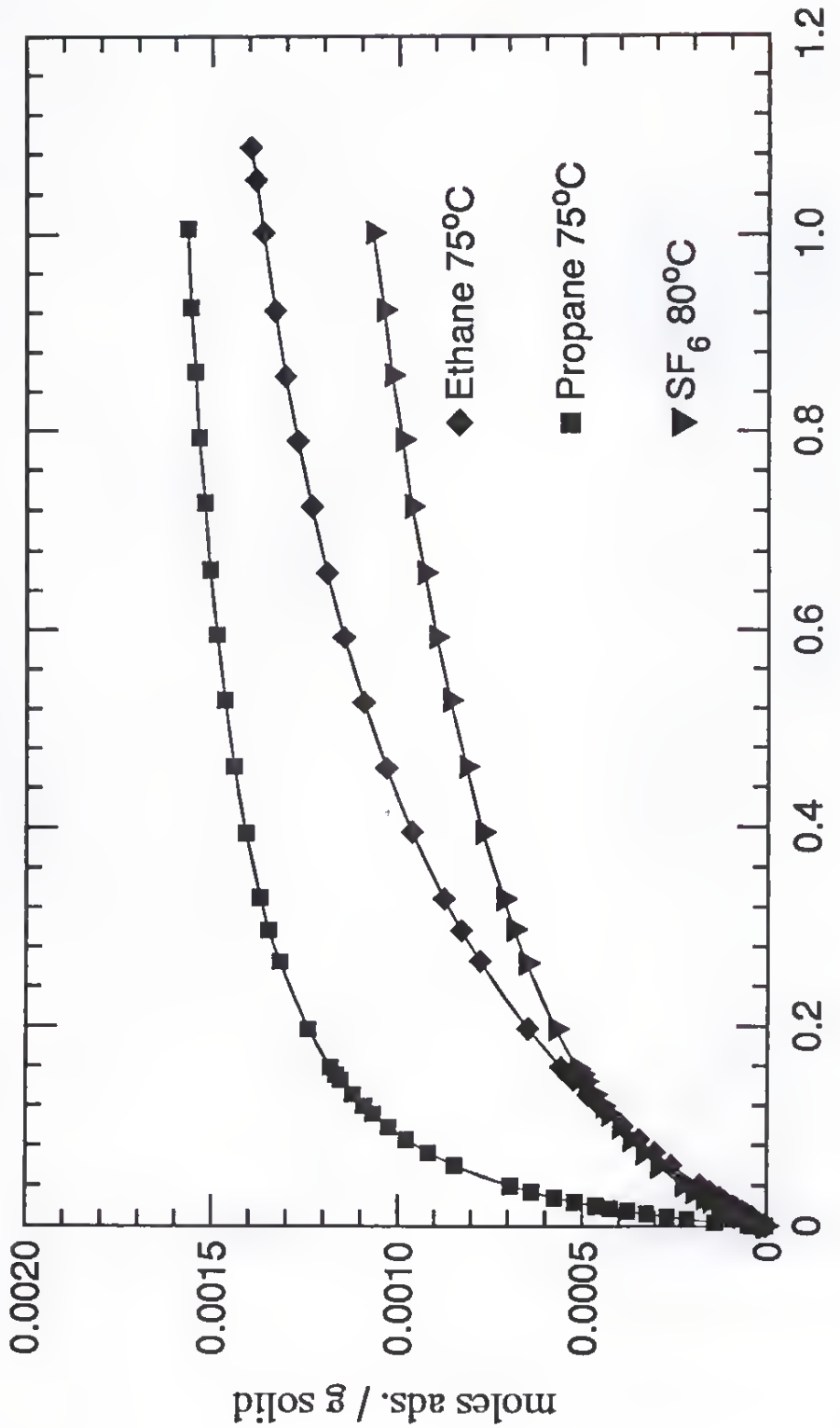

Figure 2-7: Adsorption Isotherms for the Condensible Gases Studied with HZSM-5.

interaction ($-\Delta H_1$), Process 2 for pores that were 1.5 times as large, and Process 3 for pores that were at least twice the size of the gaseous adsorbate. As described above, zeolites, or solids with a defined pore structure, present problems with this interpretation of the processes. We shall, therefore, define nomenclature to describe the adsorption of a molecule. The order of pore filling, which depends upon K, will be designated by the term Process with Process 1 corresponding to the pore that fills with greater ease. The term Type will be used to describe the matching of the adsorbate and pore dimensions. A Type 1 adsorbate is one in which the molecular dimensions of the adsorbate match the pore. A Type 2 adsorbate interacts more strongly with one wall than the rest of the pore, while a Type 3 adsorbate interacts strongly with one wall and weakly with the rest of the pore surface or with a molecule on the opposite surface. In contrast to HZSM-5, the pores of carbonaceous A-572 consist of parallel graphitic sheets or planes. The adsorbate-adsorbent interactions occur along the surface of these planes, with adsorbate-adsorbate interactions also occurring parallel to the planes. The consequences of these differences on adsorption by HZSM-5 compared to carbon will be elucidated.

The difference in the process, type designation is manifested in the thermodynamic data for adsorption for HZSM-5. Consider the two processes for the larger adsorbates SF_6, ethane and propane, which have approximately the same dimensions as the channels. The process with the more $-\Delta H$ corresponds to the process with the smaller K at elevated temperature. The calculations of Everett and Powl[22] indicate that the strength of the

Table 2-6: Enthalpies and Entropies for A572, HZSM-5, and FSG

		$-\Delta H_{1,2,3}$ kcal/mol	$-\Delta S/R_{1,2,3}$
N_2			
	A572	4.8 ± 0.01, 4.3 ± 0.2, 3.0 ± 0.2	17.8 ± 0.3, 19.6 ± 0.8, 17.1 ± 0.7
	HZSM5	4.9 ± 0.3, 3.1± 0.4	21 ± 0.5, 16 ± 0.9
	FSG	4.2 ± 0.4, 2.9 ± 0.1	20.01± 1.6, 18.4 ± 0.3
CO			
	A572	5.3 ± 0.3, 4.3 ± 0.3, 3.4 ± 0.2	18.5 ± 1.3, 18.3 ± 1.4, 18.7 ± 0.8
	HZSM5	6.1 ± 0.08,5.2 ± 0.3, 3.1± 0.5	22± 0.2, 22 ± 0.2, 15± 0.2
	FSG	4.1± 0.2, 3.6 ± 0.2	18.7 ± 0.7, 21 ± 0.72
CH_4			
	A572	6.2 ± 0.4, 5.1± 0.2, 4.0 ± 0.3	20.1± 1.8, 20.2 ± 0.9, 19.2 ± 1.4
	HZSM5	5.1 ± 0.03, 4.5 ± 0.1	18 ± 0.3, 21 ± 0.2
	FSG	4.6 ± 0.1, 3.2 ± 0.1	19.5 ± 0.3, 18.9 ± 0.5
C_2H_6			
	A572	10.2 ± 0.4, 8.1± 0.2, 6.8 ± 0.2	20.8 ± 1.3, 20.01± 0.8, 20.9 ± 0.9
	HZSM5	8.5 ± 0.2; 9.2±1.7	22.7 ± 0.7; 34.9±5.7
	FSG	5.0 ± 0.4; 5.6±0.3	16.6 ± 1.4; 22.4±0.8
C_3H_8			
	A572	12 ± 3, 9.4 ± 0.3, 8.3 ± 0.6	20.2 ± 10.2, 18.6 ± 1.1, 20.5 ±1.1
	HZSM5	9.7 ± 0.5, 12.4 ± 0.9	20.5 ± 1.3; 31.4 ± 1.3
	FSG	4.9 ±0.8, 6.8 ± 0.8	12.02 ± 2.02, 24± 2
SF_6			
	HZSM5	7.6 ± 0.3, 9.5 ± 0.006	16.5 ± 0.8; 27.4 ± 0.02
DME			
	HZSM5	22.4 ± 4.5, 13 ± 0.7; 10.6±1.3	34.6 ± 10.1; 23.6 ± 1.5; 24.3±3.0

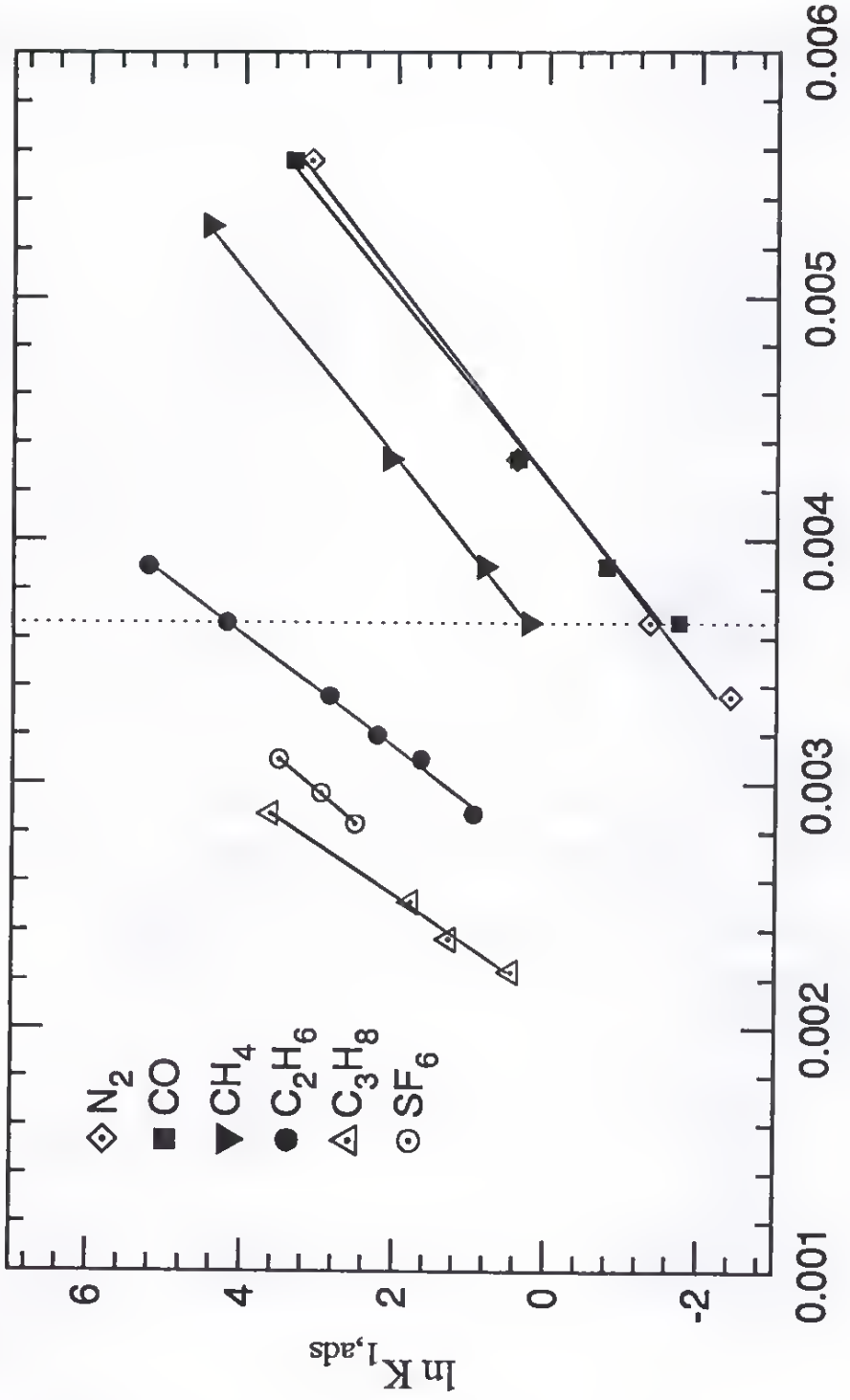

Figure 2-8: ln K_1 vs. 1/T(K) for the Gaseous Adsorbates Studied with HZSM-5.

adsorptive-solid interactions should be based on enthalpies and not upon the equilibrium constants which contain entropic contributions.[22] With the larger enthalpy assigned to the smaller zig-zag channel, the entropy associated with constraining the larger molecule in the small channel causes the equilibrium constant for adsorption for the smaller channels to decrease. Consistent with these proposals, June *et al.* report that the channels of the zeolite exhibit constraining effects upon lengthening hydrocarbon chains, such that these molecules are forced to take on a more elongated shape.[41-43] In zeolites with small channels of fixed dimensions, the entropic factors associated with the loss of rotational freedom when larger adsorbates enter the channels leads to a smaller equilibrium constant for the more strongly adsorbed molecule.

For the smaller adsorbates, N_2 and CH_4, the more negative enthalpies for Process 1, are also manifested in a larger equilibrium constant than those for Process 2. Adsorption of CO was best defined by a three process interpretation of the adsorption data. Process 1 is attributed to weak hydrogen bonding with the acid sites of HZSM-5. Although CO has a weak dipole, correlation of n_1 for CO with n_1 for DME indicates that both gases are interacting with the same number of hydrogen bonding sites. CO is weakly basic compared to DME and the magnitude of the DME interaction is evident in the enthalpy for the first process. Processes 2 and 3 for CO correspond to similar interactions observed for Processes 1 and 2 of N_2.

In order to gain further insights from the thermodynamic data, a plot of the entropy vs. enthalpy of adsorption was constructed and is shown in Figure 2-9. When data for all the processes are combined a poor correlation results. However, when the

data are divided into two sets corresponding to adsorption in the smaller and larger channels, better correlations are found. Smaller enthalpies are expected for adsorption of molecules in larger channels as generally observed. However, the need for two different enthalpy/entropy plots indicates different entropies associated with filling the two channels. This could result from the adsorbate leading to different losses of vibrational freedom for the silicon and aluminum atoms comprising the walls of the different size channels.

The following adsorptives, with the process listed in parentheses, are assigned to the smaller channels: $N_2(1)$, CO(2), $CH_4(2)$, $C_3H_8(2)$, $SF_6(2)$. The following are assigned to the larger channels: $N_2(2)$, CO(3), $CH_4(1)$, $SF_6(1)$, and $C_3H_8(1)$. Least squares lines are constructed for these two assignments in Figure 2-9. The smaller channel plot gives an excellent correlation ($R^2 = 0.99$). The Type of interaction is different for N_2 and CO than for propane and SF_6. Thus the slope of the line contains an enthalpy and entropy component from the dispersion interaction and from changing the Type of interaction. Those adsorbate processes assigned to the larger channel span a range of only four entropy units and give a poorer enthalpy - entropy plot ($R^2 = 0.66$)

For methane, the Process 1 point with the larger enthalpy falls on the large channel plot while Process 2 falls on the small channel plot. Contrary to expectation, with either assignment the enthalpy for methane binding is lower than that for N_2. The low $-\Delta S$ causes methane to pack in the small channel in a manner that gives rise to a lower enthalpy of interaction. One possibility would involve interaction of the edge instead of the face of

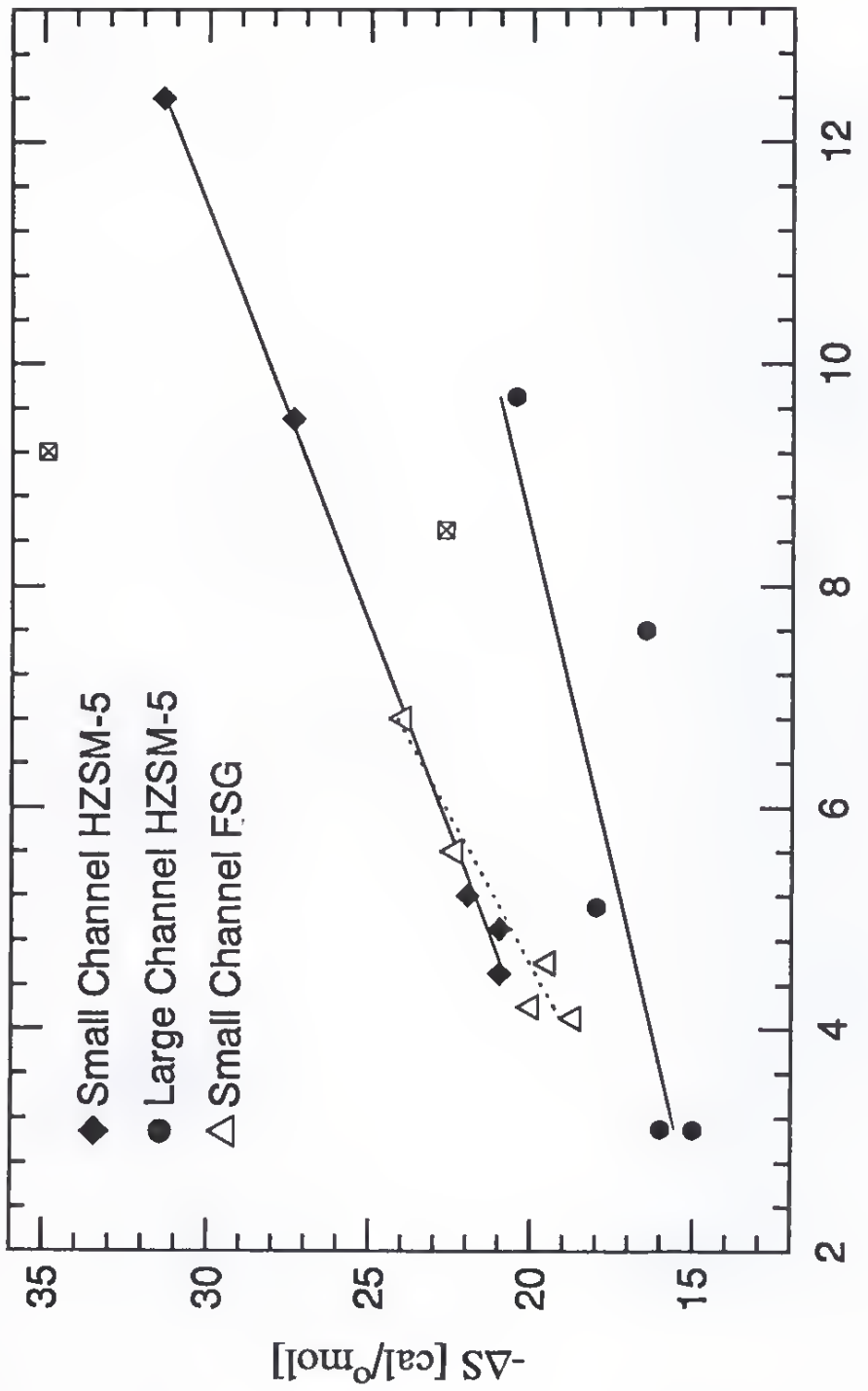

Figure 2-9: Entropy and Enthalpy Correlation for the Large and Small Channel of HZSM-5. The Correlation for the Small Channel of Silica is also shown.

the tetrahedral methane molecule with the solid surface in the small channel. This packing would lead to a smaller -ΔH and would suggest assigning Process 2 to the small channel. The methane enthalpy assigned to the larger channel (Process 1) is that expected if methane adsorbs with the face of the tetrahedron on the solid. With this assignment methane falls on both the large channel and small channel enthalpy-entropy plots.

Adsorption of ethane, like propane and SF_6, resulted in a reversal of the enthalpy-entropy assignments. Examination of the entropic term for the second process of ethane indicates a more negative contribution than propane or SF_6. If one included ethane on the above enthalpy-entropy plot, Figure 2-9, the corresponding point would lie well above the best fit line indicating a much more ordered adsorption for ethane. This can be explained by the size of the ethane molecule in relation to the channel diameter. ZINDO molecular modelling of ethane indicates that the maximum length of the molecule is 4.821 Å. The dimensions of the smaller channel are reported as 5.1 x 5.4 Å. Of the molecules examined, ethane is the only adsorbate capable of spanning the smaller channel, perpindicular to the surface, and interacting with both walls. Ethane adsorption in the larger channel is believed to occur with the bond axis of the molecule parallel to the surface in an eclipsed conformation. Further support for this will be offered in an analysis of the MEA surface areas and pore volumes, *vida infra*.

Dimethyl ether was not included in these correlations. Adding them to the enthalpy-entropy plots indicates that specific interactions are involved in Process 1 and weak hydrogen bonding in Processes 2 and 3.

Further support for the above proposals arises from a van der Waals plot. For carbon, the square root of the van der Waals, *a*, parameter plots up linearly with the Process 1 enthalpies ($R^2 = 0.99$). Figure 2-10 shows a similar plot for HZSM-5. For the smaller channel, a fair correlation results ($R^2 = 0.96$) indicating a general trend. A linear van der Waals plot is expected only if the Type of interaction is the same for all molecules involved. Thus, the slope of the plot shown has a contribution from changing the Type of interaction for the small and large molecules. This behavior is contrasted to carbon where the adsorptive selects pores from the distribution available to undergo similar adsorbate-wall interactions for all molecules involved in the i^{th} processes. This plot supports the proposals offered above in the discussion of the enthalpy-entropy plots. The small channel methane is lower than expected and the larger channel methane is higher.

A wide variety of probe molecules have been studied on carbonaceous adsorbents and none show the reversal in enthalpy and equilibrium constant shown by HZSM-5 adsorption of ethane, propane and SF_6. In contrast to HZSM-5, the pores of the carbonaceous A-572 consist of parallel graphitic sheets or planes. The adsorbate-adsorbent interactions occur along the surface of these planes, and a large adsorbate is less constrained than it is in a cylinder. This suggests that the reversal in K and ΔH is more a function of the cylindrical shape of the zeolite pores than the fixed pore size distribution. Slit shaped pores do not require the extent of adsorbate reorganization that cylindrical ones do.

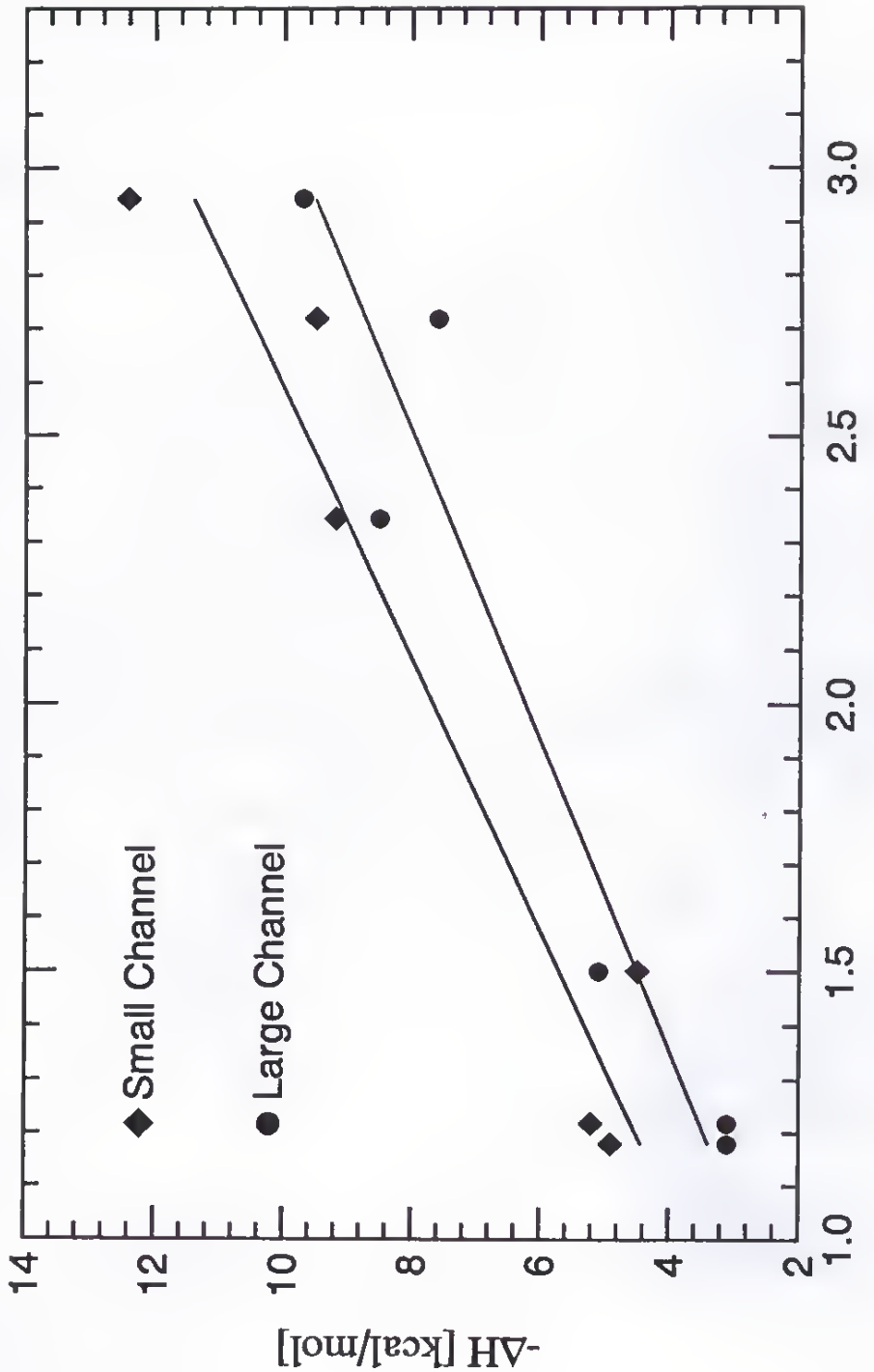

Figure 2-10: -ΔH vs. vdW [a]$^{1/2}$ for HZSM-5

Adsorption by Silica Gel

Adsorption isotherms on Fisher silica gel, FSG, are also best fit by a two process analysis of the adsorption data. Figure 2-11 shows the adsorption isotherms for the non-condensible gases studied at -44°C. The enthalpies and equilibrium constants for Process 1 with silica gel are smaller than those for HZSM-5, Table 2-7. Amorphous silica consists of larger pores the HZSM-5 and thus lacks the concentrating power found with smaller pores. These differences dramatically illustrate the influences of porosity on adsorption. The propane enthalpies suggest that the pores of amorphous silica are larger than the pores of HZSM-5. However, the N_2, CO and CH_4 enthalpies are comparable to those for the larger channel in HZSM-5 indicating that either there are small pores in FSG that are not accessed by propane or FSG has larger pores but a more polarizable surface.

Reversals in process enthalpies are observed for ethane and propane with silica gel. Although silica is amorphous, it is comprised of cylindrical pores which, as was observed for HZSM-5, invoke constraining effects on larger adsorbate molecules. This reversal in an amorphous solid supports our assignment of reversals to the channel as opposed to the slit nature of the pores. Thus, cylindrical pores exist in both amorphous silica and HZSM-5. The entropy-enthalpy plot for the small pores is given in Figure 2-9. For the adsorbates studied with silica, the enthalpies and entropies for Process 1 of N_2, CO, and CH_4 and the enthalpies for Process 2 of ethane and propane give a fair correlation. The magnitudes of the small pore enthalpies also plot up linearly with the square root of the

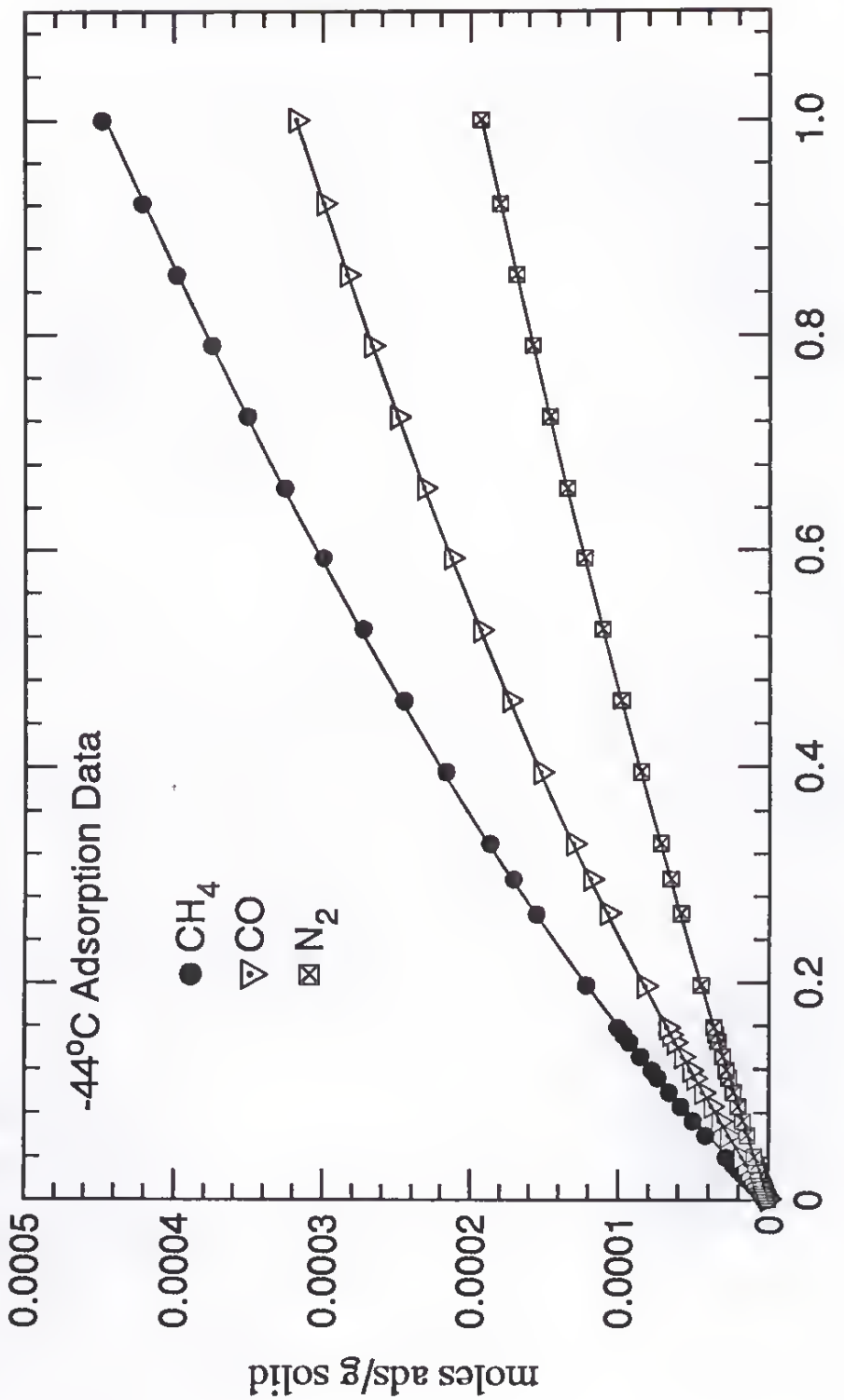

Figure 2-11: Adsorption Isotherms for the Non-Condensible Gases Studied with FSG

Table 2-7: Equilibrium Constants, *n*-values, Enthalpies, and Free Energies

N_2 / FSG				
$n_1 = 0.213 \pm 0.001$			$n_2 = 2.48 \pm 0.07$	
$-\Delta H_1 = 4.2 \pm 0.4$			$-\Delta H_2 = 2.9 \pm 0.1$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
-94	4.9±0.4	0.567	0.29±0.03	-0.436
-62	0.9±0.4	-0.015	0.09±0.03	-1.014
-44	0.5±0.2	-0.275	0.05±0.02	-1.367
-17	0.14±0.09	-1.015	0.03±0.01	-1.822
CO / FSG				
$n_1 = 0.451 \pm 0.002$			$n_2 = 2.2 \pm 0.1$	
$-\Delta H_1 = 4.1 \pm 0.2$			$-\Delta H_2 = 3.6 \pm 0.2$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
-93	7±1	0.710	0.6±0.2	-0.175
-62	1.4±0.3	0.149	0.14±0.05	-0.827
-44	0.7±0.1	-0.147	0.06±0.02	-1.265
-17	0.23±0.09	-0.739	0.03±0.02	-1.747
CH_4 / FSG				
$n_1 = 0.33 \pm 0.001$			$n_2 = 3.03 \pm 0.14$	
$-\Delta H_1 = 4.6 \pm 0.1$			$-\Delta H_2 = 3.2 \pm 0.1$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
-93	20.1±2.5	1.073	0.6±0.2	-0.185
-62	2.8±0.3	0.437	0.16±0.03	-0.765
-44	1.3±0.3	0.105	0.09±0.03	-1.074
-17	0.45±0.2	-0.408	0.04±0.02	-1.649
n_i in mmoles, K_i in atm^{-1}, $-\Delta H_i$ in kcal $mole^{-1}$				

Table 2-7 continued

C_3H_8 / FSG				
$n_1 = 0.111 \pm 0.0001$			$n_2 = 2.8 \pm 0.2$	
$-\Delta H_1 = 4.9 \pm 0.8$			$-\Delta H_2 = 6.8 \pm 0.8$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
75	2.9±0.5	0.731	0.1±0.02	-1.599
125	1.02±0.5	0.0156	0.03±0.02	-2.686
150	0.9±0.2	-0.1248	0.02±0.01	-3.444
C_2H_6 / FSG				
$n_1 = 0.284 \pm 0.002$			$n_2 = 2.3 \pm 0.2$	
$-\Delta H_1 = 5.0 \pm 0.4$			$-\Delta H_2 = 5.6 \pm 0.3$	
Temp°C	K_1	$-\Delta G_1$	K_2	$-\Delta G_2$
40	0.7±0.3	-0.022	0.08±0.04	-0.157
55	0.5±0.2	-0.045	0.05±0.02	-0.195
75	0.33±0.1	-0.083	0.03±0.01	-0.242
100	0.19±0.07	-0.123	0.018±0.008	-0.298
n_i in mmoles, K_i in atm^{-1}, $-\Delta H_i$ in kcal $mole^{-1}$				

van der Waals constant with the process reversal assignment, Equations 2-14 and 2-15. The small range in enthalpies and entropies for the larger pores of FSG precludes an analysis of the enthalpy - entropy relations or the van der Waals plot.

$-\Delta H_1 = 1.458667\ (\pm 0.09)\ a^{1/2} + 2.380663\ (\pm 0.19)$ $R^2 = 0.98$ Equation 2-14

$-\Delta H_2 = 1.163552\ (\pm 0.3)\ a^{1/2} + 1.782741\ (\pm 0.57)$ $R^2 = 0.86$ Equation 2-15

Utility of the Equilibrium Parameters

The multiple equilibrium parameters provide unprecedented detail about the adsorption process. The calculated capacities of the processes, $n_{i,ads}$, in moles and the

equilibrium constants, $K_{i,ads}$, can be substituted into Equation 2-3 , as was illustrated for carbon, to resolve the total isotherm into the Process 1 and 2 components. This resolution is shown in Figure 2-12 for CH_4 with HZSM-5 and shows that adsorption occurs simultaneously in all pores of the solid during the adsorption process.

Of particular importance are the surface areas and pore volumes for the individual processes that can be calculated from the *n*'s of the MEA using the molar volume and cross sectional area of the adsorbate as was done for carbon in the previous section. Adsorbate volumes and areas vary considerably in different literature reports and as such were calculated using ZINDO molecular modelling.[44] The molecular areas and volumes used in the determination of MEA surface areas and volumes are listed in Table 2-8. The calculated MEA accessible surface areas reported in Table 2-9 for HZSM-5 are N_2, 269 $m^2 g^{-1}$; CO, 382 $m^2 g^{-1}$; CH_4, 363 $m^2 g^{-1}$; C_2H_6, 367 $m^2 g^{-1}$; C_3H_8, 357 $m^2 g^{-1}$ and SF_6, 409 $m^2 g^{-1}$. The surface areas calculated are based on the maximum dimensions of the molecule which best represents the bulk area covered on the surface of the solid per molecule. The selected molecules will pack differently due to variations in their electronic structure so that the tetrahedral or octahedral complexes of CH_4 and SF_6 may pack tighter than the linear molecules. N_2 has the lowest surface area of the probes examined which is attributed to the strength of interaction between the gas and the solid. Methane and the remaining adsorbates are more polarizable which affords a greater surface interaction and the possibility for more adsorbate to be adsorbed.

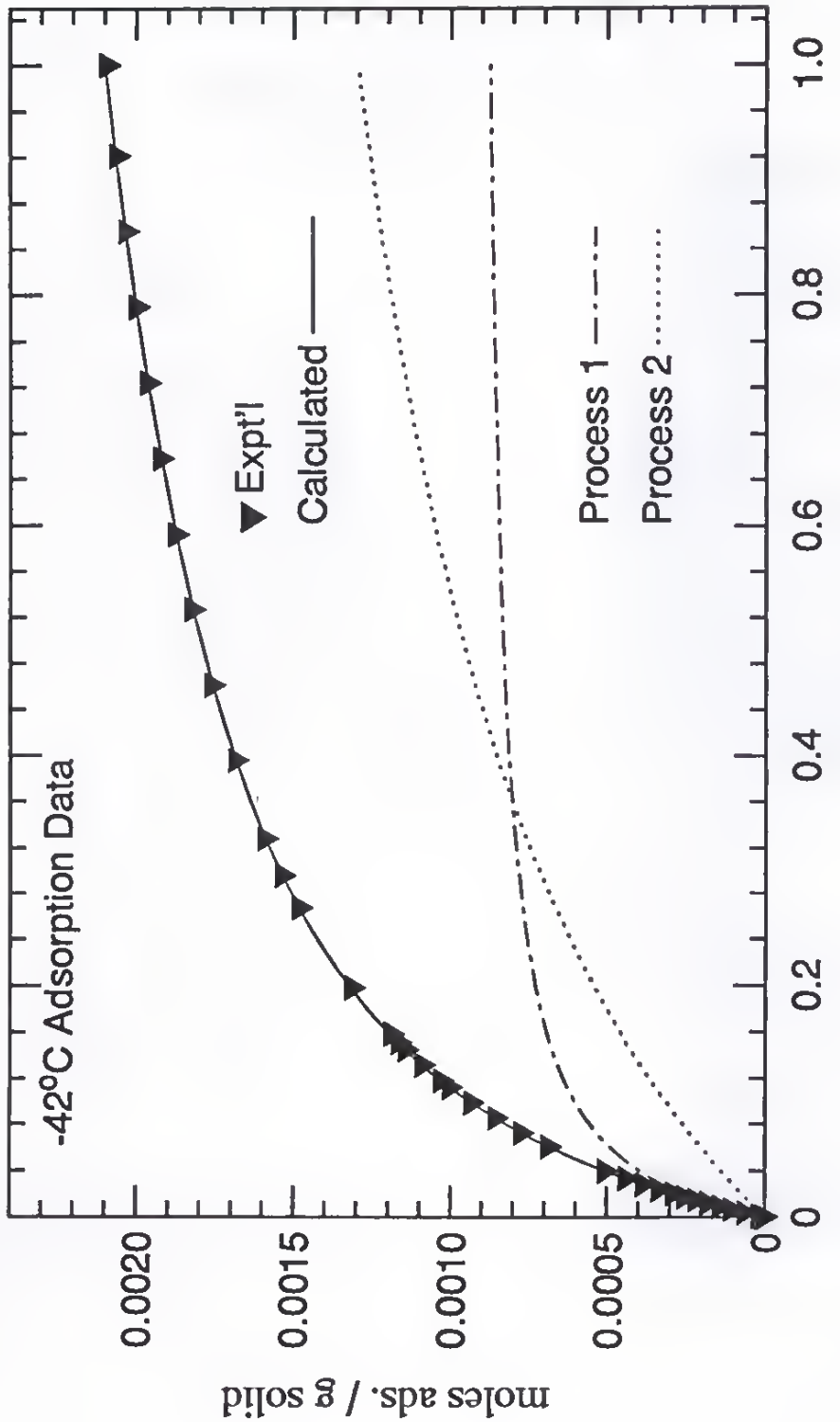

Figure 2-12: Process Resolved Isotherms for CH_4 Adsorption by HZSM-5

Ethane, as discussed earlier, is believed to span the diameter of the smaller channel perpendicular to the surface, and parallel the surface in the larger channel. In the smaller channel, ethane would have three hydrogens interacting with the solid surface on both walls. The molecular surface area for ethane in this configuration is 20.509 $Å^2$, as calculated by ZINDO. For the larger channel, ethane is expected to lay flat, in an eclipsed conformation, with four hydrogens interacting with the surface. The molecular surface area for ethane in this configuration is 25.325 $Å^2$. The calculated MEA surface

Table 2-8: ZINDO Calculated Molecular Surface Areas and Volumes for Selected Probes

	N_2	CO	CH_4	C_2H_6	C_3H_8	SF_6	DME
Adsorbed Dimensions	x by y	x by y	x by z	x by z	x by z	x by z	x by z
x_{max}	2.991	4.279	4.101	4.079 4.788	6.602	5.267	6.311
y_{max}	3.054	3.339	3.942	4.821 3.888	4.554	4.872	4.166
z_{max}	4.046	3.183	3.829	3.809 4.007	4.074	5.555	4.285
Occupied Surface Area [$Å^2$]	15.974	17.978	20.728	20.509 25.325	35.503	38.621	35.696
Calculated Molar Volume [mL mol^{-1}]	25.167	28.444	29.907	47.472 47.477	64.578	77.524	56.683

area for ethane adsorbing in the two channels as described is 367 $m^2 g^{-1}$ which is in very close agreement with the MEA surface area of methane. Correlation of this information with that presented in the enthalpy-entropy plots adds further support for MEA to distinguish pores of different dimensions and provide an accurate assessment of porosity

for porous materials. The increase in the surface area for SF_6 is attributed to its ability to overlap into the channel intersections and interact with the available surface.

The values of the surface area from MEA are only slightly lower than the value of 402 $m^2 g^{-1}$ from BET. The BET model is generally applicable to the determination of surface areas for mesoporous and macroporous solids where multilayer adsorption is possible. However, for solids with micropores, the BET is not applicable, not only for those reasons introduced in Chapter 1, but also that, in microporous materials, condensation (multilayer formation) of an adsorbate is not possible. In the absence of multilayer formation, the BET model simplifies to the Langmuir equation.[13] The MEA model is therefore applicable to the determination of surface areas for microporous materials, however, unlike Langmuir or BET, MEA is capable of resolving subtle differences in adsorption equilibria which, as for ethane, provides insight into the ordering of adsorbate molecules.

As expected, the process capacities in mmoles g^{-1} (Tables 2-5 and 2-9) decrease as the kinetic diameters of the gas molecules increase from 3.64 to 5.5 Å The reported total H-J t-plot pore volume for HZSM5 at 77K with N_2 was found to be 0.15 ml g^{-1}. Calculation of the total pore volume by the MEA (Table 2-9) for N_2 indicates a total volume of 0.07 ml g^{-1}. The other adsorptives gave values closer to 0.1 ml g^{-1}. Clearly MEA is calculating pore volumes and surface areas for HZSM-5 which are in close agreement with accepted models for determining micropore volumes. At the temperatures of porosimetry measurements, the channel intersections are expected to be filled with

Table 2-9: Resolved Process Capacities and Pore Volumes

	HZSM-5			FSG		
	N_2			N_2		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	1.542	0.038	144.25	0.213	0.0054	20.5
2	1.289	0.033	125.01	2.48	0.0624	238.5
Total	2.831	0.071	269.26	2.693	0.0678	259
	CO			CO		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	0.6089	0.0173	65.9	0.451	0.0128	48.8
2	1.22	0.0347	132.04	2.2	0.063	238.1
3	1.7	0.0484	183.99			
Total	3.5289	0.1004	381.93	2.651	0.076	286.9
	CH_4			CH_4		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	1.99	0.0595	248.32	0.33	0.0098	41.5
2	0.92	0.0275	114.8	3.03	0.0906	378.1
Total	2.91	0.087	363.12	3.36	0.1004	419.6
	C_3H_8			C_3H_8		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	0.8189	0.053	175.02	0.111	0.0072	23.7
2	0.85	0.055	181.67	2.8	0.1808	598.4
Total	1.6689	0.108	356.69	2.911	0.188	622.1
	C_2H_6			C_2H_6		
Process	mmol ads	ml ads	area[m^2g^{-1}]	mmol ads	ml ads	area[m^2g^{-1}]
1	1.92	0.091	292.72	0.284	0.0134	43.3
2	0.6	0.0285	74.05	2.3	0.1092	350.6
Total	2.52	0.1195	366.8	2.584	0.1226	393.9
	SF_6					
Process	mmol ads	ml ads	area[m^2g^{-1}]			
1	0.56	0.043	130.2			
2	1.2	0.093	279			
Total	1.76	0.136	409.2			

adsorptive making the deviation in the conventional porosimetry and MEA values for non-condensible gases even larger than those for surface area. However, analysis of the BJH desorption data for HZSM-5 indicates the presence of mesoporosity. Although HZSM-5 and other zeolites are reported microporous materials, literature reports state that under conditions of drying, ion exchange, dealumination, and deammination textural damage can develop giving rise to mesoporosity.[45]

Further analysis of the *n* values of HZSM-5 adds support for the assignment of the processes previously discussed. Examination of the process volumes for Process 1 of N_2, Process 2 of CO, and Process 2 of CH_4 indicate similar capacities, approximately 0.03 mL. This supports the assignment of methane's Process 2 to the smaller channel of HZSM-5. SF_6 indicates a larger volume than do the other probes. This can be attributed to SF_6 overlapping into the channel intersections. Based on the similarities of the total reported surface areas for CH_4, CO, ethane and propane, the MEA surface area for HZSM-5 is reported as 366 $m^2 g^{-1}$.

Likewise, examination of the volume capacities for silica indicate that all of the gases share similar volumes, except for N_2 and CO. The lower volume obtained for N_2 is attributed to its weak affinity for the surface of silica. The pore volume obtained from N_2 porosimetry was 0.32 ml. This is larger than that calculated by MEA indicating condensation in larger pores of the amorphous silica. The MEA surface area for silica with methane, ethane, and propane is in close agreement with that of BET. This is possible due to the BET calculation being performed in a pressure range of 0.05 to 0.3

torr, which would not allow for the condensation N_2. The MEA surface area of silica is reported to be 478 $m^2 g^{-1}$.

Conclusions

The MEA model presented in this chapter has made an attempt to answer some of the problems faced when interpreting adsorption equilibria. Porous materials, whether amorphous or crystalline, contain a distribution of pore sizes and surface defects which give rise to sites or processes of different adsorption potential. The MEA model provides a method for separating these adsorption processes such that an understanding of these multiple interactions can be obtained. The process capacities provide a means of calculating accessible surface areas and pore volumes based on accepted values of the area and volume of the adsorptive. Correlation of the temperature dependent equilibrium constants provides the enthalpies of interaction for the processes. The adsorption isotherm can be separated into the individual processes by substituting into Equation 2-3 the correspnding *n* and K values for a particular temperature set. Resolution of the processes allows one to see at what pressures maximum capacity for a process is reached.

The carbonaceous adsorbents discussed presented a linear correlation of the enthalpies, $-\Delta H_1$, with the square root of the van der Waals [a] parameter and polarizability for the gases studied. This led to the belief that the interactions for the different sized adsorbates were similar for Process 1 regardless of the probe. Such a relation allows one to predict, on the basis of the known van der Waals parameter or polarizability, the enthalpies or equilibrium constants for a new adsorptive. Clearly, this is

a step in the right direction for predicting adsorption isotherms for probe gases whose interactions in the pores or channels would be assumed similar to those of previously examined probes. For HZSM-5, correlation of the van der Waals parameter was not as linear as the carbonaceous adsorbents. Examination of the adsorption interactions for the different sized adsorbates revealed that linearity was close if the Type of interaction was the same. The smaller adsorbates did not interact as strongly as the larger adsorbates which approached the dimensions of the channels. Likewise, as the adsorbates approached the dimensions of the channel, entropic contributions arose as a result of the adsorbate undergoing a more ordered adsorption on the surface. These entropic contributions resulted in lower equilibrium constants for those pores where the greatest interaction (largest enthalpy) was occurring. These problems resulted in a Process, Type designation for describing the interaction of the adsorbate molecule with the pores or channels of the solid where the Process describes the ease of adsorption and the Type the matchup of the probe and pore dimensions.

Comparison of MEA surface areas and pore volumes to N_2 porosimetry indicates that MEA surface areas are generally lower than traditional BET measurements for carbon which may be a result of N_2 condensing in the larger pores of the solid . For HZSM-5, the small pore channel dimensions do not allow for molecules to aggregate preventing condensation which in turn reduces the BET equation to the Langmuir equation providing a close correlation of the two models with MEA. Traditional N_2 porosimetry measurements at 77K do not adequately describe the adsorption process since normal applications of these materials occur at or above ambient temperatures. Multiple

temperature analyses provide a better description and allow for a better correlation of the adsorption data with known parameters of the solids and related adsorptives. Ratioing of the areas of tested probes and related surface areas affords the prediction of process capacities and surface areas for untested probes.

The MEA model is capable of presenting useful information in gas-solid equilibria based on the general principles of thermodynamics. Many of the important properties which are not easily obtained from current adsorption and surface area models which should be considered in selecting appropriate adsorbent systems can be obtained from this model based on the well defined physical properties of the adsorbates.

CHAPTER 3
COMPETITIVE ADSORPTION FROM CYCLOHEXANE

Introduction

Porous materials including carbon, silica gel, and zeolites are used in many practical applications with liquids including separation and purification as well as catalysts supports. In order to understand the competitive binding involved in these applications, a fundamental understanding of the relevant equilibria is necessary. An MEA analysis of gas-solid equilibria for several probe gases examined with porous carbonaceous and silica based adsorbents was discussed in Chapter 2. Adsorption isotherms were resolved into three adsorption processes for the adsorbates studied with the carbonaceous adsorbent, Ambersorb® 572. In the absence of specific interactions, the first process corresponded to adsorption of the probe into the smallest accessible pores of the solid, and the second process to pores with larger diameters. Silica gel indicated the presence of two adsorption processes for the adsorbates examined. In our study of gas-solid equilibria, dispersion type forces dominated the adsorption of nonpolar gaseous probes by the carbonaceous and silica based adsorbents. To extend the applications of the Multiple Equilibria Analysis (MEA) model further,[46] the competitive adsorption of liquid probes from dilute solution with silica gel and the carbonaceous adsorbent Ambersorb®572 (A-572) were investigated.

Adsorption from solution involves several different molecular interactions which are shown in Figure 3-1. A_1 and A_3 represent the affinity of the solid for adsorption of

solute and solvent respectively, and A_2 is the interaction of the solute with the solvent. A_2 is related to the solubility of the solute in the solvent and, for non-interacting systems, is related to the difference in the solubility parameters. Both A_1 and A_3 involve interactions with the accessible surface area of the solid and are influenced by the adsorbate and solvent nonspecific London dispersion interactions, dipole-dipole interactions, and donor-acceptor interactions. In the case of a porous adsorbent with little donor-acceptor functionality, A_1 and A_3 are dominated by nonspecific London dispersion interactions for nonpolar adsorbates and dipole induced dipole interactions for polar adsorbates which are usually larger. These forces correlate typically to the enthalpy of vaporization (ΔH_v) of the adsorbate.

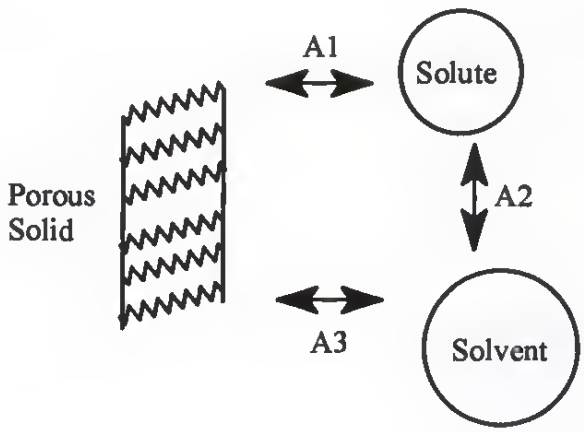

Figure 3-1. Model for Liquid Adsorption in Porous Solids

This work investigates the tendency of A-572 and silica gel to preferentially adsorb a donor solute from a dilute binary solution. The acidic sites on the surface of silica gel

lead to specific donor-acceptor interactions which are larger than the non-specific interactions described above. Previously, the Cal-Ad[47] method was able to elucidate three hydrogen-bonding sites of different strengths when pyridine was used as the basic probe molecule. In order to extend the applications of the MEA model and to investigate the competitive interactions (A_1, A_2, and A_3) of an acceptor solid such as silica gel to preferentially adsorb specific donor type molecules, several dilute binary systems have been investigated and are reported here. The preferential adsorption has been interpreted using the MEA model to obtain equilibrium constants ($K_{i,\,ads}$) for adsorption to the surface of silica gel and A-572.

Experimental

Materials. Silica Gel, FSG, (Fisher S-679, lot # 934403) was obtained from Fisher Scientific and Ambersorb®572 (A-572, lot# 2201) was obtained from Rohm and Haas. Both solids were dried in a vacuum-oven at room temperature for 24 hours prior to use. The FSG is a porous, amorphous solid with a surface area of ~570 $m^2 g^{-1}$ with an average pore size of 28 Å as determined from the N_2 isotherm at 77K using a 5 point BET calculation[25] and the BJH desorption isotherm.[35] FSG contains micropores (0.02 mL g^{-1}) and mesopores (0.33 mL g^{-1}) as determined by nitrogen porosimetry. A-572 is a carbonaceous adsorbent with a surface area of 1100 $m^2 g^{-1}$ and a total pore volume of 1.1 ml g^{-1}, and is comprised of micro- and mesopores. Gas-solid measurements were performed on a Micromeritics ASAP 2000 gas-solid analyzer. Probes and solvents were

cyclohexane (certified ACS spectroanalyzed), pyridine, benzonitrile, nitrobenzene, p-xylene, benzene and chlorobenzene.

UV/VIS spectroscopy. All UV/VIS spectra were measured using either 1.0 or 0.1 cm quartz UV cells in a Perkin-Elmer Lambda 6 UV/VIS spectrophotometer.

Adsorption measurements. Approximately 0.22 to 0.23 g of silica or A-572 was precisely measured into 12 vials. A 1.00 mL aliquot of known concentration of probe in solvent spanning a desired concentration range was then pipetted over the solid. The vials were sealed and wrapped with parafilm, and the samples were allowed to equilibrate for 16-24 hours with occasional agitation. The equilibrium concentration of the probe in solution was determined from calibration curves of absorbance versus concentration. In order to correct for errors incurred from large dilutions, absorbance measurements were made from two or more separate dilutions and an average value recorded.

The total number of moles of probe adsorbed per gram of solid adsorbent, n, was calculated using Equation 3-1.

$$n = \frac{(C_i - C_{eq})V(0.001L/mL)}{m} \qquad \text{Equation 3-1}$$

where C_i is the initial probe concentration (mol L^{-1}), C_{eq} is the equilibrium probe concentration (mol L^{-1}), V is the volume of solution added (mL), and m is the mass of adsorbent (g). Total adsorption isotherms were obtained by plotting n vs. C_{eq} for each sample vial.

Equilibrium analyses. The measured isotherms were analyzed with a multiple process equilibrium analysis model for porous solids which was described in Chapter 2. The equilibrium expression derived in earlier studies of gas-solid equilibria is shown in Equation (3-2) where SA is the total number of moles of solute adsorbed per gram of solid, n_i, is the capacity of process i in moles, $K_{ads,i}$ is the equilibrium constant of adsorption for process i, and C_{eq} is the equilibrium solute concentration in solution. The two parameters, n_i and $K_{ads,i}$, are calculated using a modified simplex routine designed to fit measured equilibrium concentrations and [SA]for a series of probe concentrations to multiple equilibrium equations. The number of processes used in the fit was either 1 or 2 depending on the minimum needed to obtain a good data fit.

$$[SA] = \sum_i \frac{n_i K_i [Ceq]}{1 + K_i [Ceq]} \qquad \text{Equation 3-2}$$

Results and Discussion

Adsorption from cyclohexane. In this work, various probe molecules were studied in the same solvent. Cyclohexane was selected as the solvent since it is a non-polar, poorly solvating solvent. These properties minimize the solute-solvent interactions (A_2). Using the same solvent keeps A_3 constant for all of the systems investigated. The probe liquids used in the adsorption measurements were selected to encompass a range of

Table 3-1: Summary of Solutes and Cyclohexane and Physical Properties[48]

Probe Liquid	MW [g/mol]	Polarizability [Å^3]	van der Waals [a]	Dipole Moment [Debye]	Molar Volume [mL/mol]	S'' [a]	E_b [b]	C_b [b]	ΔH_v [kcal/mol]
Pyridine	79.10			2.22	80.9	2.44	1.78	3.54	8.39
Benzonitrile	103.12	12.5	33.39	4.18	102.1	2.63	1.65	0.75	11.0
Nitrobenzene	123.11	12.9		4.22	102.9	2.63	1.27	0.57	13.2
Benzene	78.11	10.3	18.00	0	89.4	1.73	0.70	0.45	7.34
p-Xylene	106.17	14.1	30.93	0	122.6	---	---	---	8.60
Chlorobenzene	112.56	12.3	25.43	1.69	101.7	2.07	---	---	8.73
Cyclohexane	84.16	11.0	22.81	0	108.0	1.11	0	0	7.16

electrostatic and covalent donor properties. In order to study the possibility of π-interactions of the weak donor probes with the surface, various substituents on the benzene ring were used to influence the basicity of these interactions. Properties of these materials are summarized in Table 3-1.

Adsorption isotherms. Figure 3-2 shows the adsorption isotherms for various solute molecules adsorbed from cyclohexane solvent by silica gel. Except for benzene and chlorobenzene, all of the solutes studied produced non-linear isotherms which required two processes to obtain a data fit that was within the accuracy of the measurements. One process was sufficient to describe the adsorption of benzene and chlorobenzene. The points in Figure 3-2 correspond to the experimental data, and the curves drawn through the data are generated from the best fit equilibrium analysis. The experimental data points and the calculated values for each point are presented in Appendix E.

Table 3-2 summarizes the n and $K_{i,ads}$ parameters for all of the isotherms where n is the capacity of the solid for the adsorption process in number of millimoles per gram of solid , and $K_{i,ads}$ is the adsorption equilibrium constant which is a measure of the affinity of the probe for the solid. Since silica gel is an acidic solid, $K_{1,ads}$ for all of the adsorbates refers to the affinity of the probe for the strongest adsorption sites. $K_{2,ads}$ refers to the potential for multilayer adsorption of the adsorbate and adsorption to weaker surface sites. It should be emphasized that the $K_{i,ads}$ values correspond to an average value of different processes that have K_{ads} values close enough to be treated as a single process in the data work up within experimental error of the measurement. V_1 and V_2 correspond to the volume of solute adsorbed via process 1 and 2. These are obtained from the product of

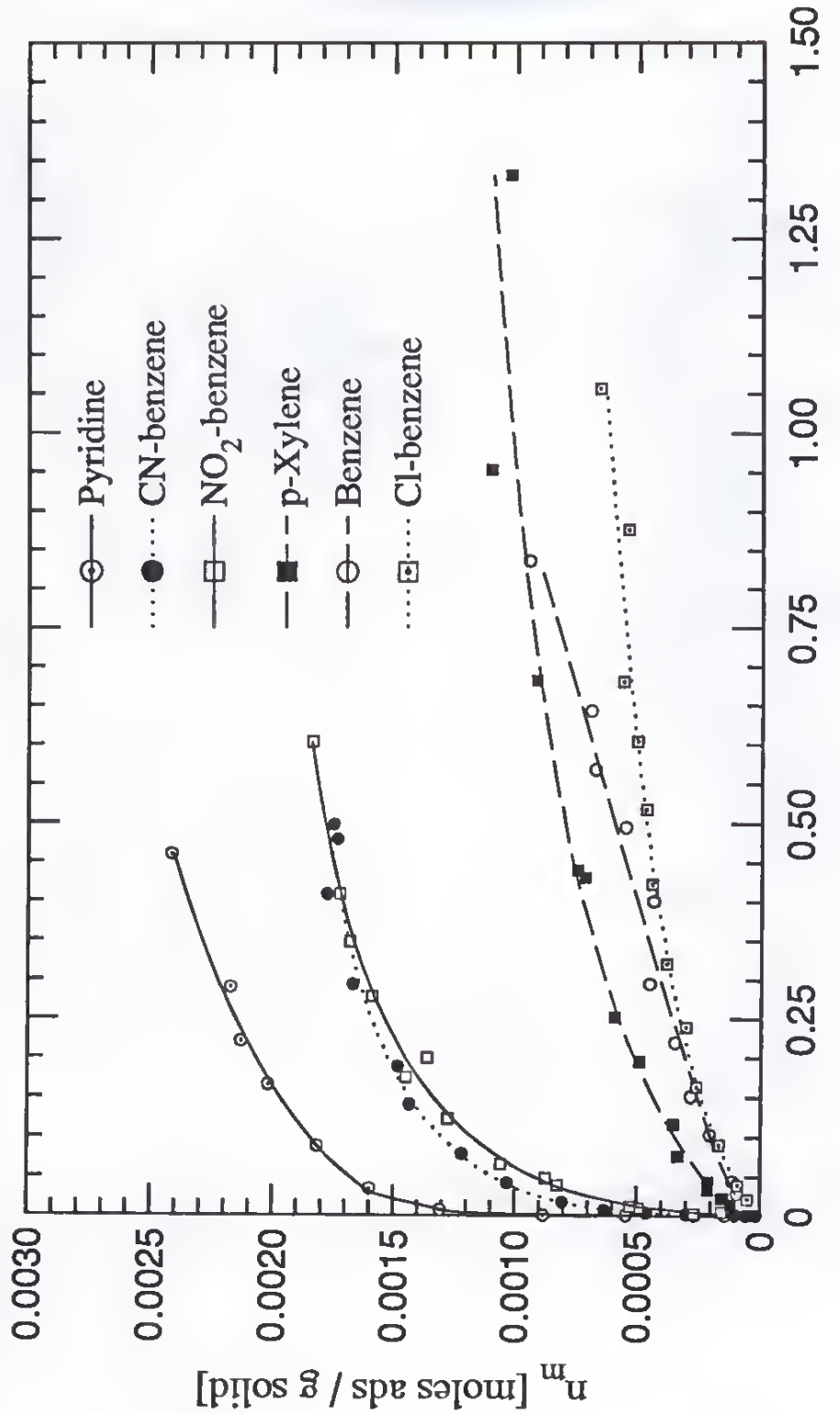

Figure 3-2: Adsorption Isotherms for Selected Adsorbates with Silica Gel.

Table 3-2: Adsorption Parameters for Adsorption from Cyclohexane by Silica Gel.

Probe	$K_{1,ads}$	n_1 [mmol]	$V_{1,ads}$ [mL]	$K_{2,ads}$	n_2 [mmol]	$V_{2,ads}$ [mL]
Pyridine	577±159	1.58±0.6	0.128	2±149	1.67±10.6	0.135
p-Xylene	235±10	0.12±0.04	0.015	2.2±0.8	1.3±0.5	0.162
Benzonitrile	224±50	0.9±0.2	0.092	6±37	1±7	0.121
Nitrobenzene	108±19	0.7±0.1	0.072	5±9	1±2	0.152
Chlorobenzene	2.5±0.2	0.85±0.08	0.086			
Benzene	0.7±0.3	2.3±0.8	0.206			

the molar volume (mL mol^{-1}) of the solute and the calculated capacities, n_i expressed in moles.

Considering the adsorption of the various probes on the surface of silica gel, pyridine has the greatest affinity and benzene the smallest affinity for the strongest sites on the surface. The ordering of $K_{1,ads}$ is readily explained by the donor strength of the adsorbate and the resulting solute-solid interactions. When silica is the solid, A_1 is influenced by donor-acceptor interactions between the probe molecule and the surface. Of the probes examined, pyridine was the most basic and is represented by the largest $K_{1,ads}$. P-Xylene experienced the second highest $K_{1,ads}$ followed by benzonitrile, nitrobenzene, chlorobenzene and finally benzene. Of these probes, pyridine, benzonitrile and nitrobenzene normally react via the basic lone pairs of electrons. The basicity of these lone pairs determines their ability to undergo acid-base interactions. Benzene, chlorobenzene and p-xylene normally hydrogen bond through the pi system of the aromatic ring. The order of the equilibrium constants for K_1 indicates that, as expected, the electron donating ability of the methyl groups of p-xylene increases the basicity of the

aromatic pi system over that of benzene and chlorobenzene.[49] Nitrobenzene interacts with the acidic sites of silica through the nitro group. The interaction of nitrobenzene is weaker than that of benzonitrile. Interaction through the pi system is not expected to occur as the basicity of the pi system for nitrobenzene is reportedly less than that of the nitro group.[49] Chlorobenzene has a slightly greater equilibrium constant than benzene. The lone pairs of electrons on chlorine may contribute to the basicity of chlorobenzene and allow for weak hydrogen bonding interactions with the acidic sites of silica. The pi donor, benzene exhibited the weakest adsorption affinity of the probes examined.

As was described in Chapter 2, the van der Waals [a] parameter describes the relative attraction between like molecules. A plot of the square root of this parameter with the ln K_1 should give a slope corresponding to the relative attraction between the probe and the solid. However, such a plot is valid only for those adsorbates undergoing non-specific adsorption interactions with the adsorbent. In minimizing the contributions of A_3 shown in Figure 3-1, the adsorption of the selected adsorbates was performed in the same solvent such that the adsorbates experience the same type of competitive adsorption. Subtraction of the van der Waals parameter for the solvent from the vdw [a] parameters of the probes has been suggested, however this only subtracts a constant and does not affect the parameter which is more greatly affected, K_1. Correlation of the ln K_1 with square root of the van der Waals [a] parameter for benzonitrile, benzene, p-xylene and chlorobenzene resulted in an R^2 of 0.87. This is shown in Figure 3-3. The increasing order of K_1 for silica does not follow the order of increasing van der Waals parameter of the probe molecules as was observed for the gaseous adsorbates previously reported.

Therefore the correlation of the van der Waals [a] parameter with ln $K_{1,ads}$ is not appropriate for predicting equilibrium constants for the interaction of new donor adsorbates with silica.

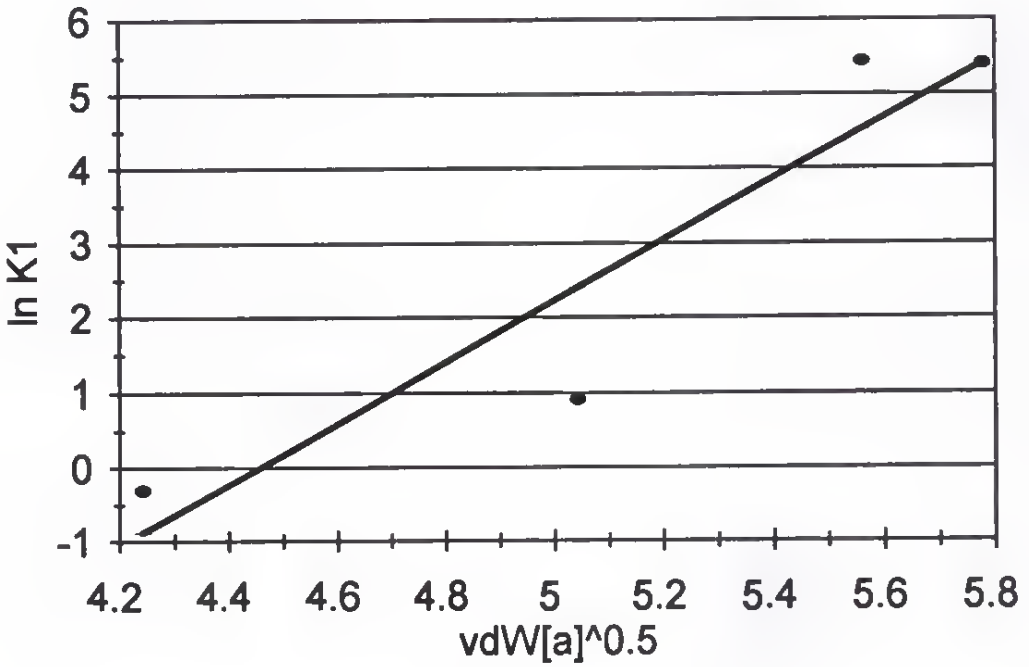

Figure 3-3: ln K_1 vs. vdW[a]$^{1/2}$ for benzonitrile, benzene, p-xylene and chlorobenzene.

The E and C model has been developed to describe the electrostatic and covalent contributions of donors and acceptors in acid-base interactions.[50] Although this is a very limited data set, an ECW analysis of silica with the adsorbates whose E_B and C_B parameters are known resulted in an E_A of 6.37 (± 1.78) and C_A of -0.20 (± 0.57) with W = -4.34 (± 2.1), and an R^2 of 0.95. The equation is shown below, Equation 3-3. The E

and C model is a dual parameter model; however, within experimental error, C_A for silica is zero. Therefore, electrostatic forces are dominating the interactions of the selected adsorbates with silica.

$$\ln K_1 = 6.37 (\pm 1.78) E_B - 0.20 (\pm 0.57) C_B - 4.34 (\pm 2.1) \qquad \text{Equation 3-3}$$

The $K_{i,ads}$ values characterize the adsorptive properties of different solids and different adsorbates. Since $\ln K_{1,ads}$ increases with increasing E_B for those adsorbates whose E_B values are known, (Table 3-1) the affinity of a solid for different adsorbates may be predicted from the electrostatic component of the adsorbate donor character. Correlation of the E_B parameters with $\ln K_1$ for pyridine, benzonitrile, nitrobenzene and benzene resulted in an R^2=0.94 and is shown in Figure 3-4.

Examination of the equilibrium constants for the second adsorption process, $K_{2,ads}$, with E_B of pyridine, benzonitrile, nitobenzene and benzene resulted in a poor correlation. However, examination of $\ln K_{2,ads}$ with the heat of vaporization for pyridine, p-xylene, benzonitrile and nitrobenzene indicates a linear relationship. A least squares analysis of $\ln K_{2,ads}$ with the $-\Delta H_{vap}$ resulted in an R^2 of 0.95. Therefore, after the adsorbates have interacted with strongest acid sites of silica, the remaining adsorption corresponds to multilayer formation in the pores of the solid.

In contrast to the adsorption parameters observed for silica, Ambersorb® 572 experiences slightly different interactions with the probes examined. A-572 is an amorphous solid whose structure, like other carbonaceous adsorbents, has been

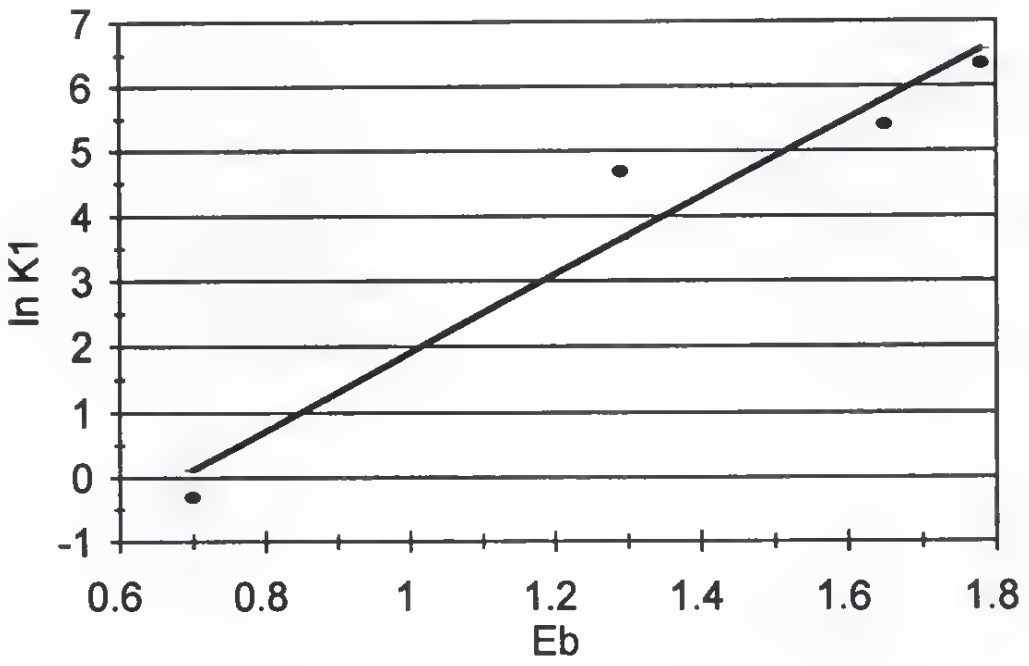

Figure 3-4: Relationship of ln $K_{1,ads}$ with E_B of the selected adsorbates studied with silica.

described as an extended array of aromatic rings comprising a slit-shaped pore geometry. Table 3-3 lists the adsorption equilibrium parameters and Figure 3-5 presents the adsorption isotherms for the liquid adsorptives examined with A-572. From Table 3-3 it is clear that the affinities of the selected adsorbates are not the same for A-572 as were found for silica. Two adsorption processes were found to best define the adsorption isotherms for the probes selected, except for benzene. Adsorption of pyridine by A-572

was characterized by a weaker K_1 than for silica indicating the absence of any strong acid sites. Benzonitrile and chlorobenzene adsorption exhibited the strongest affinity for adsorption, more so than with silica, while benzene exhibited the weakest. An E and C analysis of A-572 with the probes listed in Table 3-3 is given in Equation 3-4.

Table 3-3: Adsorption Parameters for A-572

Probe	$K_{1,ads}$	n_1 [mmol]	$V_{1,ads}$ [mL]	$K_{2,ads}$	n_2 [mmol]	$V_{2,ads}$ [mL]
Benzonitrile	6350±12	0.5±0.1	0.050	32±3	1.7±0.3	0.174
Chlorobenzene	1102±8	0.43±0.04	0.044	8±3	1.3±0.4	0.131
Nitrobenzene	314±15	1.1±0.1	0.110	14±7	2±1	0.206
Pyridine	300±260	0.5±0.4	0.041	3±38	3±4	0.245
Benzene	0.8±1	6±9	0.513			

$$\ln K_1 = 9.94\ (\pm 0.18) - 1.58\ (\pm 0.06) - 6.40\ (\pm 0.21) \qquad R^2 = 0.999 \qquad \text{Equation 3-4}$$

For A-572, electrostatic interactions are found to be stronger. Clearly, the strength of the interactions involved in the adsorption of the selected adsorbates does not follow that of their basicity, or E_B parameter. A least squares analysis of $\ln K_1$ with E_B for benzonitrile, nitrobenzene, pyridine and benzene resulted in an R^2 of 0.77.

Examination of the square root of the van der Waals [a] parameter with $\ln K_1$ for benzonitrile, benzene and chlorobenzene resulted in an R^2 of 0.9. If one examines Table 3-1, the increasing values for the van der Waals [a] parameter follows the increasing order of the K_1 values reported in Table 3-2, except for benzene. In the study of adsorption of

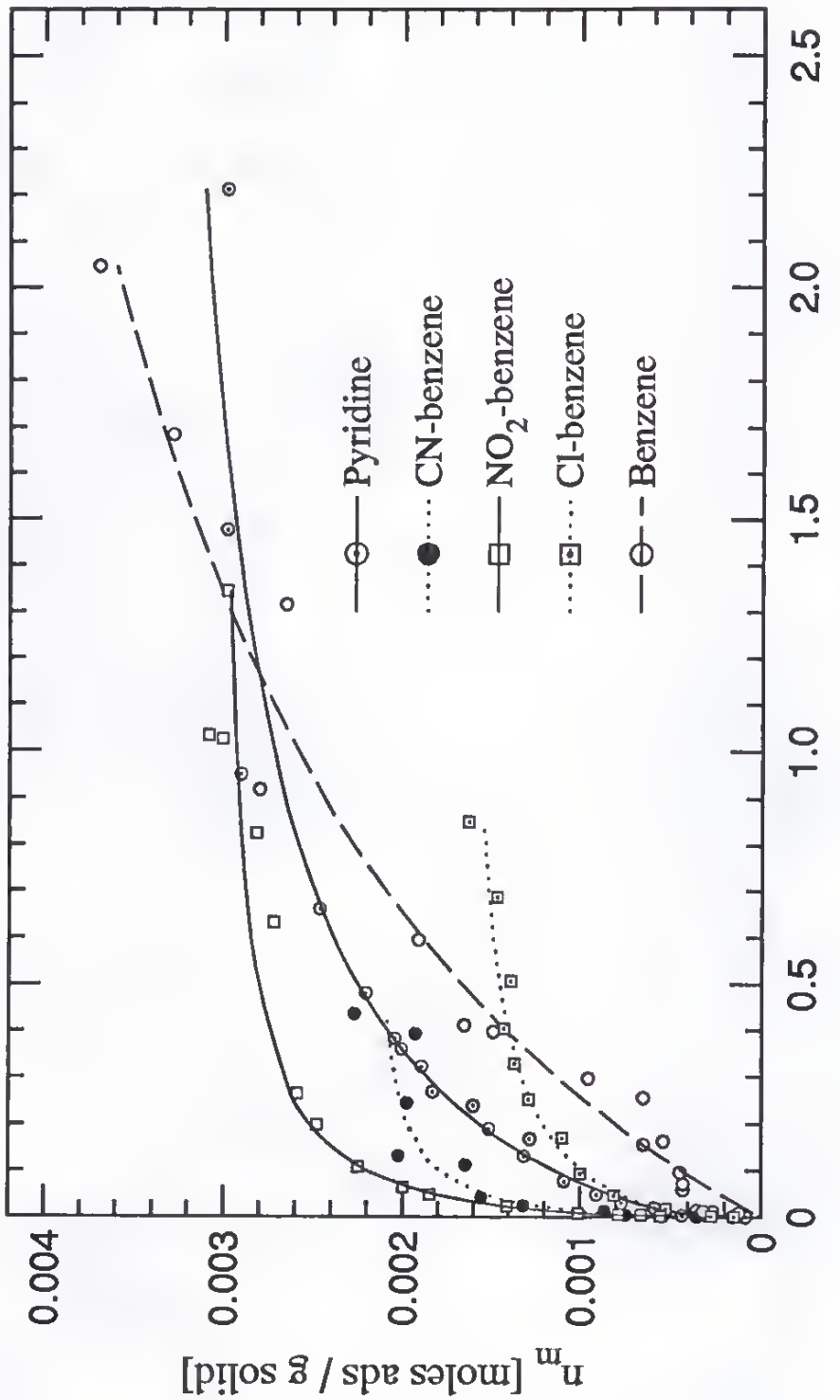

Figure 3-5: Adsorption Isotherms for Selected Adsorbates with A-572.

these probes from cyclohexane, all of the probes except benzene have a greater van der Waals [a] parameter than the solvent. This would indicate a stronger attraction for cyclohexane by A-572 thereby making it difficult for benzene to displace the solvent. This indicates that for the carbonaceous adsorbent, nonspecific dispersion forces are dominating the adsorption process.

Examination of the equilibrium parameters for the second adsorption process of A-572 indicates slightly larger adsorption interactions are occurring in carbon than were observed for silica. Examination of ln $K_{2,ads}$ with the enthalpy of vaporization of the adsorbates results in a poor correlation ($R^2 = 0.4$). Therefore, the interactions of the second process relate to adsorption of the probe molecules in pores approximately 1.5 times the size of the adsorbate. This was illustrated in Chapter 2 where the multiple adsorption processes observed for A-572 with gaseous adsorbates resulted in a set of equilibrium constants of which the largest equilibrium constant, K_1, referred to adsorption into the smallest accessible pores which closely matched the size of the adsorbate. The second largest equilibrium constant referred to adsorption of the gaseous adsorbates into pores which were approximately 1.5 times the size of the adsorbate, and the smallest K_{ads} referred to pores which were roughly twice the size of probe. The adsorption of the gaseous adsorbates, as well as the liquid adsorbates studied here, have increasing equilibrium constants which relate linearly to an increase in the van der Waals [a] parameter for the corresponding probes. Although this data set is very limited, a general trend can be established for the prediction of the affinity of new adsorbates with A-572 based on the known van der Waals constants of the new probe.

The n values calculated for the adsorption processes relate to the number of acid sites available or accessible to the various probe molecules. For silica gel, pyridine had the largest n_1 and is interacting with the strong and weak sites of the solid. Benzonitrile, nitrobenzene, and chlorobenzene share similar capacities, and volumes for the first process which may involve the interaction of these probes with the strong sites of the solid. P-xylene is slightly bulkier with respect to the methyl groups which may prevent its accessibility to smaller pores that may contain the majority of the stronger acid sites thus contributing to its low capacity and pore volume for process 1. Within the experimental error of those probes having a second process, the volume adsorbed corresponded to approximately 0.15 mL. In comparison, the volume capacity of silica for the adsorbates examined in Table 3-2 is larger than that found in gas adsorption studies where the average volume capacity was 0.06 mL g^{-1}. This indicates the presence of multilayer adsorption on the surface of silica.

Analysis of n_1 for A-572 (Table 3-3) indicates that pyridine, benzonitrile and chlorobenzene share similar capacities. The capacity of nitrobenzene is approximately twice that of the other probes. Due to the reported slit-shape pore geometry of carbonaceous adsorbents, chlorobenzene, benzonitrile and pyridine would have easier access to smaller pores, whereas nitrobenzene may encounter difficulty with the nitro group forcing it to seek larger pores. Benzene, whose van der Waals attraction parameter is less than the solvent, encountered difficulty in displacing cyclohexane and resulted in large errors in its calculated capacity. Likewise, comparison of the volume capacity for gaseous adsorbates examined with A-572 indicates a striking similarity to the volume

capacity of the liquid adsorbates studied here. This indicates that in the liquid or gaseous state, adsorbate molecules are accessing the same pores.

Conclusions

The affinity of various donor molecules for adsorption from cyclohexane solvent by silica gel and a carbonaceous adsorbent has been compared using a MEA interpretation of the equilibrium data. The K_{ads} values obtained from an MEA fit give an indication of the donor-acceptor properties of a solid which can be used to one's advantage in selecting adsorbents to purify liquid mixtures. This information will serve to provide an indication as to the potential purity that can be achieved in the separation of a mixture. If K_{ads} values of two materials for a solid are comparable, it would be difficult to get an acceptably pure product stream. However, two materials with K_{ads} values which are orders of magnitude apart should provide a very good separation. Furthermore, this information is useful in catalytic applications in which a support should be chosen which will have a preference for adsorbing a reactant over a product. This would lead to a greater reactivity since the solid would continuously adsorb reactant molecules on the catalyst surface and displace product molecules. For silica based adsorbents, correlation of the E_B and C_B parameters, if known, for new donor probe molecules can provide an estimate of the adsorption equilibrium constant for that new probe. For carbonaceous adsorbents whose interactions are dominated by non-specific, dispersion type forces, prediction of adsorption affinities for new probes can be accomplished by the van der Waals [a] parameter. However, care should be taken when selecting solvents for the analysis of liquid adsorption if

carbonaceous adsorbents are the solids of interest so that competition between the solvent and probe can be minimized.

Clearly, more probe molecules are needed to provide a better assessment of the adsorption properties of these selected adsorbents and adsorbates by the MEA model. Such a limited data set can only provide an indication of the adsorption potential of these adsorbents for donor molecules. Further studies of liquid-solid adsorption equilibria by the MEA model are currently underway.

CHAPTER 4
SYNTHESIS AND CHARACTERIZATION OF SOL-GEL DERIVED SOLID ACIDS

Introduction

Liquid acids, such as H_2SO_4 and HF, have been used extensively for hydrocarbon cracking, isomerization, and alkylation reactions in the production of petroleum and specialty chemicals.[51-55] The need for the products of these reactions results in many tons of liquid acid waste being generated each year. Storage and transportation of acid and acid waste is costly and has fueled debate over environmental and safety concerns in their use.[56]

A solid acid capable of performing the same function as a liquid acid, which provides an ease of product isolation and is stable and regenerable at moderate to high temperatures has many environmental, as well as financial benefits.[57] Solid acids generally consist of a functionalized support matrix which contains an active complex that enhances the acidity of the support. The active complex can be of a Bronsted or Lewis nature.[55] Zeolites, aluminosilicates, are solid acids which are used in many petrochemical applications.[13,16] The acidity of zeolites is a result of Lewis acid centers generated from the incorporation of aluminum (III) in the tetrahedral matrix of silica (IV).[13,55] The aluminum is tetrahedrally coordinated in the silica matrix generating a negative charge which is balanced by a cation. Unlike many other metal - oxide systems, zeolites are

crystalline solids which have defined pore and channel sizes. This benefits those reactions where size exclusion is important. Zeolites occur naturally, but many of the more useful types are synthesized in the laboratory which is costly, in both time and in money.[13]

Silica is one of the most widely studied materials for use as a catalyst support.[12] Silica gel itself is an acid whose acidity, although weak, is derived from the hydrogen bonding of neighboring silanol groups which comprise the surface of the solid. The density of these hydrogen bonding sites give rise to weak, moderately strong, and strong acid sites. Chronister and Drago[47a] identified these acid sites in a Cal-Ad analysis of a commercial silica gel, Figure 4-1.

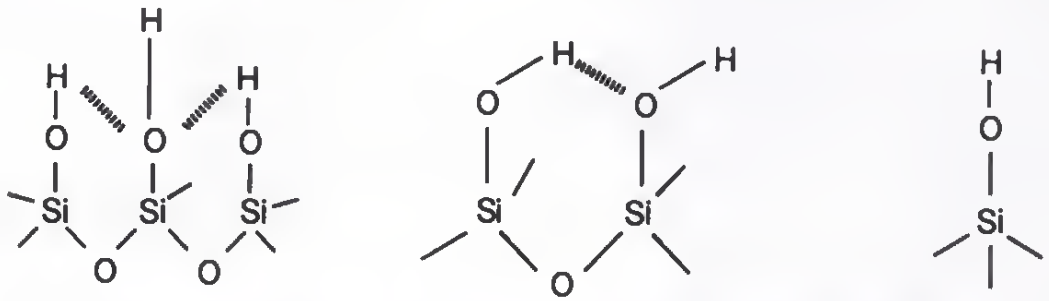

Figure 4-1: The Strong (left), Moderately Strong (Center) and Weak (right) Acid Sites of Silica Gel.

The strongest acid site was found to have a calorimetric heat of interaction of 12 kcal mole^{-1} with pyridine.

Enhancement of the acidity of silica gel was described by Getty and Drago who, by reacting $AlCl_3$ with silica gel in CCl_4, found that a complex of the type shown in Figure 4-2 could be produced.[58] A calorimetric investigation of the solid resulted in a heat of interaction of ~ 50 kcal mole^{-1} with pyridine.

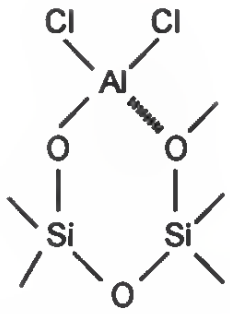

Figure 4-2: Bronsted Acidity Generated from the $AlCl_3$ / Silica Gel Catalyst

The -$AlCl_2$ is a Lewis acid drawing electron density away from a silanol OH bond resulting in a weakening of this bond, thus increasing the acidity of the proton. The result is the generation of a strong Bronsted acid site. Although a large increase in acidity was achieved, exposure to moisture resulted in deactivation of the solid.

Kob attempted to replace the sensitive -$AlCl_2$ with a sulfated WO_3 complex.[59] Although effective, difficulties with migration and clumping of the WO_3 on the surface coupled with the loss of sulfate, and the difficulty with regeneration resulted in a loss of catalyst activity after each use. Incorporation of an active complex into the matrix of the solid to minimize migration and loss of the active complex was deemed necessary.

The sol-gel method is a convenient and effective procedure for incorporating metal oxides into a silica matrix. The sol-gel procedure involves the hydrolysis, condensation, and polymerization of a silicon alkoxide to yield silica gel.[60-66] The most common silicon alkoxide used is tetraethyl orthosilicate, TEOS. A standard silica sol-gel synthesis requires approximately five steps. Hydrolysis, Step 1, of a silicon alkoxide involves the exchange of the alkoxy groups for hydroxyl groups resulting in the formation of silicic

acid. Alcohol solvents are generally used to aid in the miscibility of the TEOS and water.[66,67] The alcohol is usually similar to the alkoxy groups being displaced, although mixed alcohol systems are possible.

$$Si(OEt)_4 + 4\ H_2O + EtOH + \text{acid / base catalyst} \rightarrow Si(OH)_4 + 4\ EtOH \qquad \text{(Step 1)}$$

The hydrolysis reaction can be either acid or base catalyzed.[66,67] The choice will have an impact on the nature of the porosity and surface area of the solid. Acid catalyzed reactions generally result in small pore, high surface area materials, whereas base catalyzed reactions develop an excess negative charge in solution resulting in larger pore, lower surface area solids.[12]

Condensation, Step 2, of the silicic acid results in branching and polymerization with the formation of water.

$$Si(OH)_4 + Si(OH)_4 \rightarrow (HO)_3 - Si - O - Si(OH)_3 + H_2O \qquad \text{(Step 2)}$$

When the reaction species have polymerized, the free flowing liquid becomes a viscous, non-flowing gel, Step 3. The gel is aged, Step 4, for a period of time at a controlled temperature to ensure complete hydrolysis of the alkoxy groups. Most sol-gel reactions are carried out in sealed vessels under autogenaceous pressure. If one desires, a monolithic solid[68] can be obtained by using a vessel lined with a material which has a low affinity for wetting, such as teflon. This minimizes the stresses that develop due to

adhesion to the vessel surface if pyrex is used. After aging, the gel is dried, Step 5, in a calcination oven at temperatures ranging from 300°C to over 500°C with flowing air or oxygen to remove any residual organic material.

One advantage of sol-gel derived silicas over those produced by commercial means is that the syntheses are carried out at, or near, ambient temperatures and that relatively pure solids can be obtained.[69] Another advantage is the ability to incorporate additional metal-oxo complexes within the silica matrix. By incorporating these complexes into the structure, one is capable of controlling the relative acidity, catalytic activity, and physical properties of the solid. The control of porosity and surface area is important for effective catalytic and adsorption systems. Solids consisting mostly of large pores generally have low surface areas, whereas smaller pores increase the overall surface area and concentrating power of the solid. This is useful for systems where reactants must be concentrated around a catalyst. For silica gel systems, increasing the surface area is also a means of generating more acid sites on the solid. To control the pore size of the solid, drying control chemical additives, DCCAs, can be used.[68,70-71] These additives are generally organic bases, such as formamide, which undergo hydrogen bonding with the forming silanols of the reaction. A more uniform pore size can be established by evenly dispersing the reagents throughout the reaction mixture. Once the solid is obtained, the drying control additive is removed by solvent washing or calcination.

The incorporation of organic spacers has also been used to control the porosity of solids.[72-75] Through a modified Grignard experiment, organic compounds such as phenyl and biphenyl rings are placed between silicon atoms, Figure 4-3. This yields a route to

controlled pore size with the possibility of adding functional groups which may further enhance the reactivity of the solid.

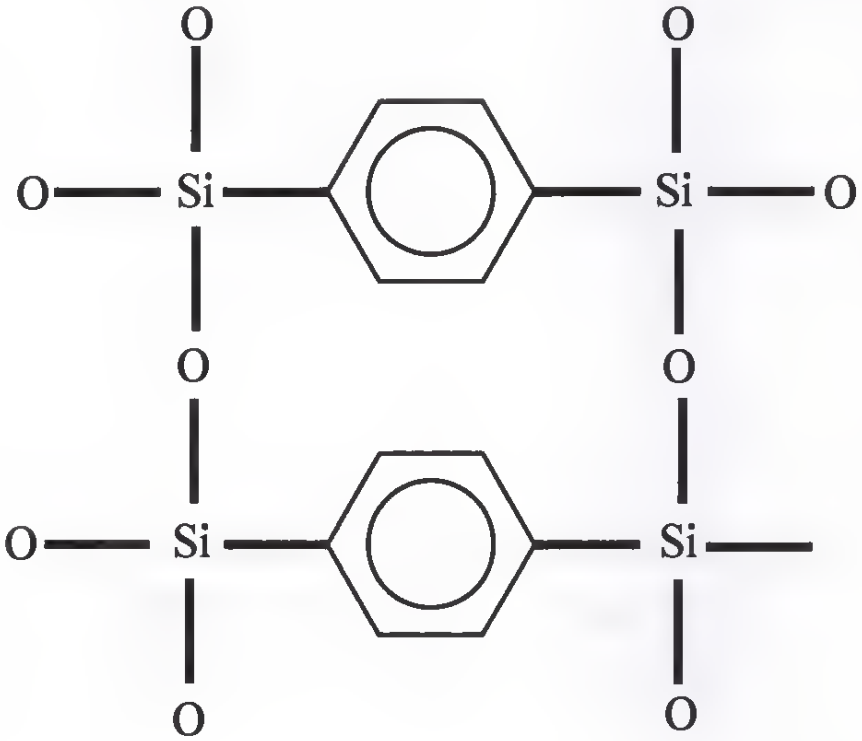

Figure 4-3: Organically Bridged Silica Gels

Mixed metal oxides, similar to those presented by Kob, can be synthesized by the sol-gel route.[76-78] By incorporating these complexes into the silica matrix, the problems observed with the tungsten catalysts may be avoided. Preliminary results for a sulfated silica gel synthesized by the sol-gel method which has the potential of extended MTBE production is described here.

Experimental

Standard Sol-Gel

In most cases an 8:1:3 ratio of H_2O, TEOS, and ethanol was used. A water to silicon ratio of 8:1 is reported to be adequate to obtain the shortest gelation time and to ensure complete hydrolysis of the alkoxide ligands.[60] To 30ml of TEOS (98%, Aldrich Chemical) was added 23 ml of 95% ethanol (AAPER Alcohol and Chemical, Co.), and 1 ml of concentrated HNO_3 (Fisher Scientific). The reaction mixture was allowed to stir in a Pyrex crystallizing dish, or a teflon cup, for 10 minutes before the addition of 18 ml of de-ionized water. The mixture was stirred an additional 15 minutes before being placed in an isothermal oven (80°C) to gel and age. After a 24 hour drying period, the resulting solid obtained is crushed and sieved through a 60 mesh screen to obtain a uniform particle size. This is followed by calcination in air at 350°C to remove any residual organic material.

DCCA Sol-Gels

The use of drying controlled chemical additives, DCCAs,[68, 70-71] and organic spacers in the synthesis of sol-gel silicas to control the porosity and surface area was performed as follows: To 30 ml of TEOS (Aldrich) was added 23 ml of 95% ethanol, 1 ml of concentrated HNO_3 (Fisher Scientific), and 10 ml of formamide (Fisher Scientific). The reaction mixture was stirred for 10 minutes followed by the addition of 18 ml of de-ionized water. Stirring was continued for another 15 minutes before being placed in an isothermal oven at 80°C. After a 24 hour period, the solid obtained was crushed and sieved before calcination in air at 350°C to remove the drying control additive.

Phenyl and Biphenyl Bridged Silicas

1,4-bis(triethoxysilyl) benzene: 1,4-bis(triethoxysilyl) benzene was prepared as described in the literature.[73-75] To 15 g of magnesium metal turnings was added 450 mL of TEOS, 300mL of THF, and 1 crystal of iodine. The reaction solution was then heated to reflux. To this was added dropwise, over a two hour period, 48 g of 1,4 - dibromobenzene (Aldrich) in 100mL of THF. This was allowed to continue refluxing for an additional hour after the addition was complete before allowing to cool to room temperature. THF was removed by vacuum distillation from the resulting grey-green solution. Two hundred milliliters of n-hexane was added and the resulting solution was filtered to remove the remaining magnesium metal. The n-hexane was removed by vacuum distillation and the resulting oil was doubly distilled under vacuum to yield a clear, colorless liquid. The resulting liquid is then combined with water, ethanol, and an acid catalyst, as described above, to promote gelation and formation of the phenyl bridged solid.

4, 4'-bis(triethoxysilyl) biphenyl: Preparation was reduced to 1/4 scale of the reported literature synthesis.[73-75] To 25 g of 4, 4'-dibromobiphenyl (Aldrich) was added 200 mL of THF, 125 mL of TEOS, 10 g of magnesium metal, and one crystal of iodine. The reaction solution was then heated to reflux under an argon atmosphere. After cooling, the THF was removed by vacuum distillation and 200 mL of n-hexane was added. The solution was filtered under argon and the n-hexane removed by reduced pressure. The remaining brownish-yellow oil was doubly distilled under vacuum to yield a clear,

colorless oil. The resulting solution was subjected to the afore mentioned sol-gel preparation and the solid obtained characterized by N_2 porosimetry and calorimetry.

Vapor Deposition of SO_3

A Schlenk tube containing a 3 g sample of pre-dried (100°C, vacuum) sol-gel silica was connected by a valved sidearm to a round bottom flask containing fuming sulfuric acid (Aldrich Chemical). The Schlenk tube was degassed while the fuming sulfuric acid was warmed to near boiling by a heating mantle. After evacuating the Schlenk tube for 30 minutes, the valve was opened and the acid vapor was allowed to equilibrate with the solid for approximately 5 minutes. The valves were then closed and the solid sample was evacuated and backfilled with N_2 and moved to an inert atmosphere dry box.

Sol-Gel Derived Sulfated Silicas

In a teflon lined autoclave was added 30 ml TEOS, 23 ml EtOH, 15 ml $SO_2(OEt)_2$ (Aldrich), and 1ml of concentrated H_2SO_4 (Fisher). The mixture was allowed to stir for 15 minutes before the addition of 18 ml of de-ionized water. Stirring was continued for an additional 15 minutes before the autoclave was sealed and placed in an isothermal oven at 80°C. The reaction was carried out for 3 days before the monolithic solid obtained was dried. The solid was crushed, followed by calcination in air at 400°C for 12 hours. The solid was allowed to cool for 3 hours open to the laboratory atmosphere before being placed in a N_2 atmosphere dry box. Substitution of $SO_2(OEt)_2$ by equal molar amounts of H_2SO_4 and $NH_4^+SO_4^{2-}$ was also performed. Samples consisting of 10% and 30% $SO_2(OEt)_2$ were also synthesized.

Characterization of Solids

N_2 Porosimetry

Characterization of commercial and sol-gel derived solids was performed on a Micromeretics® ASAP 2000 gas-solid analyzer equipped with chemisorption and physisorption software. Surface area and pore volume data was obtained from the N_2 isotherm at 77K. Surface areas were determined from a 5 point Brunauer-Emmet-Teller, BET, calculation.[25] Micropore volumes were determined from the Harkins-Jura t-plot model with thickness parameters from 5.5 -9.0 Å.[34] The Barrett-Joyner-Halenda (BJH) desorption curve was used for calculating meso- and macropore volumes.[35] All calculations were carried out using the ASAP 2000 software. Sample loadings were on the order of 0.3 g and were dried at 200°C under vacuum for a minimum of 8 hours prior to study.

Calorimetric Analysis

In order to ascertain the solid's acidic strength, calorimetric titrations with pyridine were performed and the results compared with previous solid acids. One gram samples of commercial and sol-gel derived solids were titrated with 0.3M pyridine / cyclohexane solutions. Cyclohexane was chosen because it is a poorly solvating and a poorly coordinating solvent. The solids were dried under vacuum at 200°C and stored in a N_2 dry box prior to examination. Cyclohexane, 100 ml, (Fisher reagent grade distilled over P_2O_5) was added to the calorimetric cell to create a slurry with the solid. Injection of the pyridine solutions was performed using a Hamilton gas tight syringe with calibrated stops. After each injection the heat of interaction between the solid and pyridine was measured.

The calorimeter cell is a 100 ml, silvered, double-walled vacuum flask equipped with a heater coil and thermistor. The thermistor is calibrated prior to each experiment and is connected through a digital / analog converter to a computer which calculates the heat of interaction.

Adsorption Studies

Adsorption of pyridine from cyclohexane was combined with calorimetric data to yield a combined Cal-Ad[47] analysis. Such an analysis provides information about the quantity, equilibrium constant for binding, and the enthalpy of interaction for the various types of sites on the solid. The adsorption experiment is similar to the calorimetric analysis in that the same solvent to solid ratio is used. UV-VIS measurements were made on a Perkin-Elmer Lambda 6 UV-Vis spectrophotometer at a wavelength of 252 nm with 0.1 cm quartz cuvettes. The total number of moles of probe adsorbed per gram of solid adsorbent, n, was calculated using Equation 4-1.

$$n = \frac{(C_i - C_{eq})V(0.001L/mL)}{m} \qquad \text{Equation 4-1}$$

where C_i is the initial probe concentration (mol L^{-1}), C_{eq} is the equilibrium probe concentration (mol L^{-1}), V is the volume of solution added (mL), and m is the mass of adsorbent (g). Total adsorption isotherms were obtained by plotting n vs. C_{eq} .

Thermogravimetric, InfraRed, and Carbon, Hydrogen, Nitrogen Analyses

Thermogravimetric analyses were conducted on a DuPont 2000 TGA. Typical heating rates were 10°C per minute ranging from ambient to 1000°C. IR studies were

carried out using Nujol mulls with a Nicolet 5PC FT-IR. Carbon, hydrogen and nitrogen analyses were performed by the University of Florida Elemental Analysis Laboratory.

Results and Discussion

The synthesis of metal free silicas can be easily accomplished by the sol-gel method. Sol-Gel silicas, on average, have a higher surface area and a more uniform pore size than commercial samples purchased for this study. Table 4-1 lists the surface area and porosity data for the commercial and synthesized solids studied. Table 4-1 also shows that for those solids where a drying control additive or organic spacer was used, the reported BET surface area is maintained above 700 $m^2 g^{-1}$. Table 4-1 lists three samples which were synthesized using formamide as a drying control additive. Although surface areas for these samples are maintained above 700 $m^2 g^{-1}$, variations in the surface area and pore size are a result of different drying temperatures. The following temperatures were used in drying these samples: JM93, 90°C; JM117, 120°C; JM119, 100°C. Surface areas and pore volumes could have been maintained in a tighter range had the complete experiment been performed in sealed reaction vessels over a period of several days. As was the case for these samples, the complete reaction was performed in an open crystallizing dish which allowed for the rapid loss of solvent as soon as the reaction was placed in the drying oven. The gelation times for these samples were greatly effected, and as a result so was the overall porosity. It is during the gelation stage that the final pore structure of the solid is formed. For samples JM101 and JM89, the biphenyl and phenyl bridged silicas, reactions also were performed in open vessels at 80°C which facilitated the

rapid loss of solvent and water. In the absence of a DCCA or organic spacer, synthesized silicas had surface areas ranging from 400 to almost 1000 $m^2 g^{-1}$. Samples JM4 and JM99 were standard silicas produced without the aid of a drying control additive or spacer with drying temperatures of 80°C. The average pore size calculated for these solids using N_2

Table 4-1: N_2 Porosimetry Data for Commercial and Sol-Gel Derived Silicas

Sample ID	Surface Area ($m^2 g^{-1}$)	Total Pore Volume (cc/g)	Micropore Volume (cc/g)	Avg. Pore Diameter (Å)
Formamide and Organic Spacer Controlled Silicas				
JM93	890	0.48	0.1	24
JM117	940	0.80	0.002	40
JM119	975	0.61	0.045	28
JM101	823 (4,4'-biphenyl)	0.50	0.01	28
JM89	885 (1,4 - phenyl)	0.42	0.12	19
Commercial and Standard Sol - Gel Silicas				
Davison	265	1.1	----	175
Fisher (934403)	570	0.35	----	28
JM4	948	0.5	0.08	22
JM99	457	0.2	0.15	17

porosimetry indicates that most solids consist of small mesopores averaging 26 Å in diameter. However, like the samples described above, the synthesis of these samples was performed in open vessels which facilitated the rapid loss of solvent when placed in a drying oven. The availability of commercial silicas with small pores and high surface areas is limited and at times costly. Figures 4-4 and 4-5 show the pore distributions for the Fisher and Davison commercial silicas used in this study based on the amount of N_2

adsorbed at 77K as a function of pore size. The dashed line in the figures represents 17 Å which is the limit of our instrument to accurately define micropores. In general, the commercial samples studied consisted of a range of pore sizes varying from small to very large mesopores.

In Chapters 2 and 3, adsorption of gaseous and liquid adsorbates for the commercial Fisher silica gel represented here were best defined by a one process interpretation of the adsorption data with weak affinities for those adsorbates undergoing non-specific adsorption interactions. Compared to the adsorption of similar adsorbates by carbonaceous adsorbents, multiple adsorption processes were found to exist as a result of a distribution of small and large pores resulting in strong affinities for those adsorbates which closely matched the size of the pores. Controlling the porosity of solids allows one to develop an efficient adsorbent for catalytic applications. Small pores may result in diffusional problems, as well as restrict accessibility to active sites, whereas large pores will not have appreciable concentrating power to bring reactants near the catalytic sites.

Silica, as mentioned in Chapter 3, is an acidic solid whose acidity is dependent on the number and proximity of surface hydroxyl groups. With silica, an increase in the surface area results in an increase in surface hydroxyl functionality. The density of these hydroxyl groups facilitates the presence of strong and moderately strong acid sites. Calorimetric investigation into the acidities of commercial and sol-gel silicas indicate similar enthalpies of interaction of the solids that correspond to 12 - 15 kcal $mole^{-1}$ with pyridine for the strongest site. Figure 4-6 shows the calorimetric titration curve for commercial and sol-gel silicas. Samples with higher surface areas, and a greater number

of acid sites, interact with more pyridine as demonstrated by the greater total heat evolved as a function of the millimoles of base added.

The acid sites for many metal oxides are composed of the simple hydroxyl group. For solids with a low density of these acid sites, an increase in surface functionality can be achieved through aqueous washings of the solid with 30% H_2O_2 followed by several washings with aqueous HCl.[79] Washing the solid in this manner results in the breaking of Si-O-Si, or Metal-O-Metal, bonds and the formation of additional Si-O-H, or M-OH bonds. For low surface area solids, such as the commercial Davison silica with a surface area of 275 $m^2 g^{-1}$ and an average pore diameter of 175 Å, the effects of the peroxide washing may not increase the surface functionality much more than that present in the starting material. Figures 4-7 through 4-9 show the effects of peroxide washing on commercial and sol-gel silicas. Peroxide washing of sol-gel silicas resulted in a large increase in the total number of acid sites compared to the commercial silica samples of Fisher and Davison studied. Minor changes in the reported surface areas and pore volumes were observed after washing the sol-gel silicas with peroxide as indicated in Figure 4-9.

Sulfonation of metal oxides such as ZrO_2 and SiO_2/ WO_3 has been reported to increase the acid strength of these solids.[59,60] General sulfonation methods include washing the solid with copious amounts of aqueous H_2SO_4. However, for some solids washing with acid promotes the aggregation of the metal oxide resulting in an inactive complex. Sulfonation of silica gel by fuming sulfuric acid is also a convenient method for

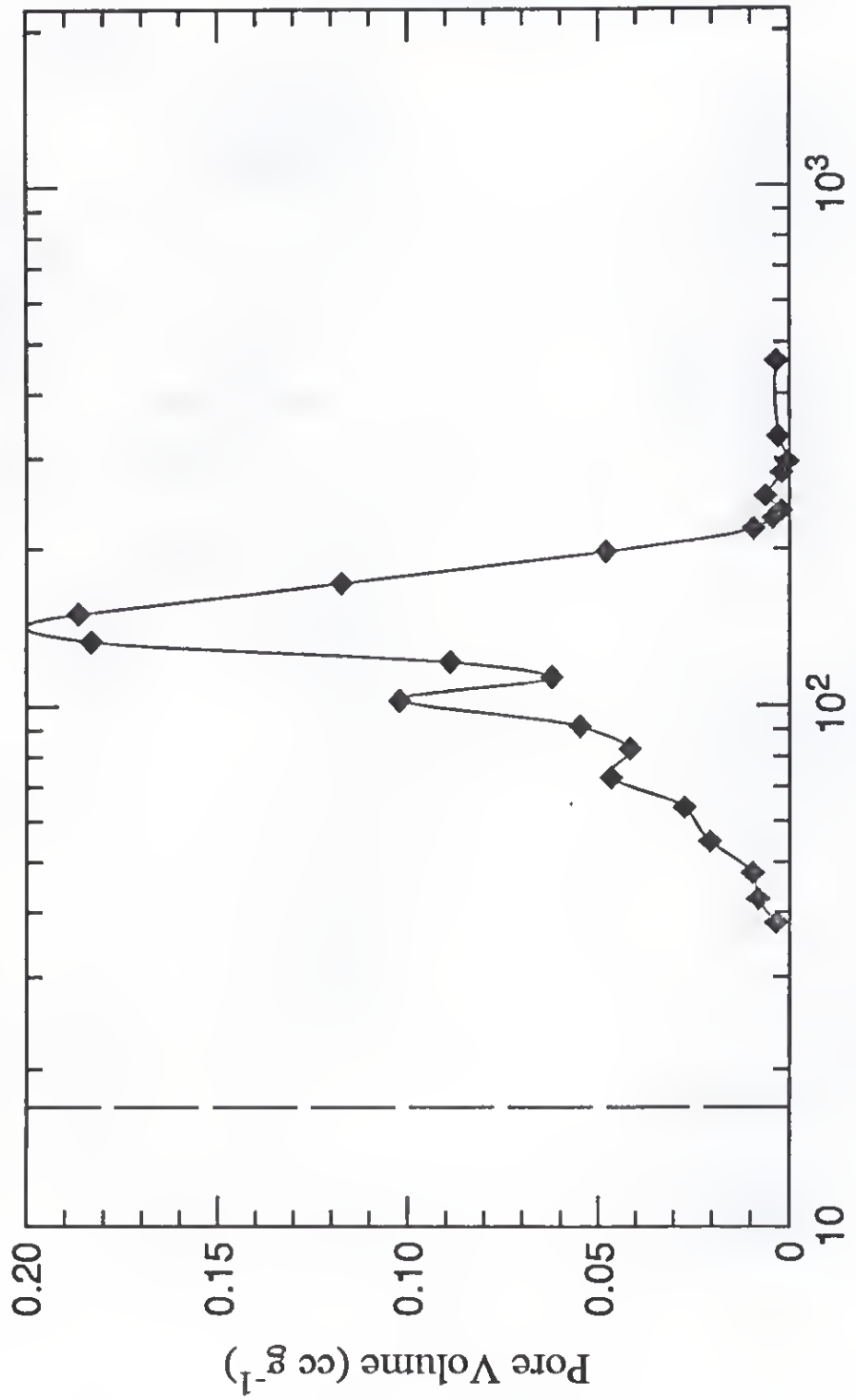

Figure 4-4: Pore Size Distribution for Davison Silica Gel. The dashed line represents 17Å.

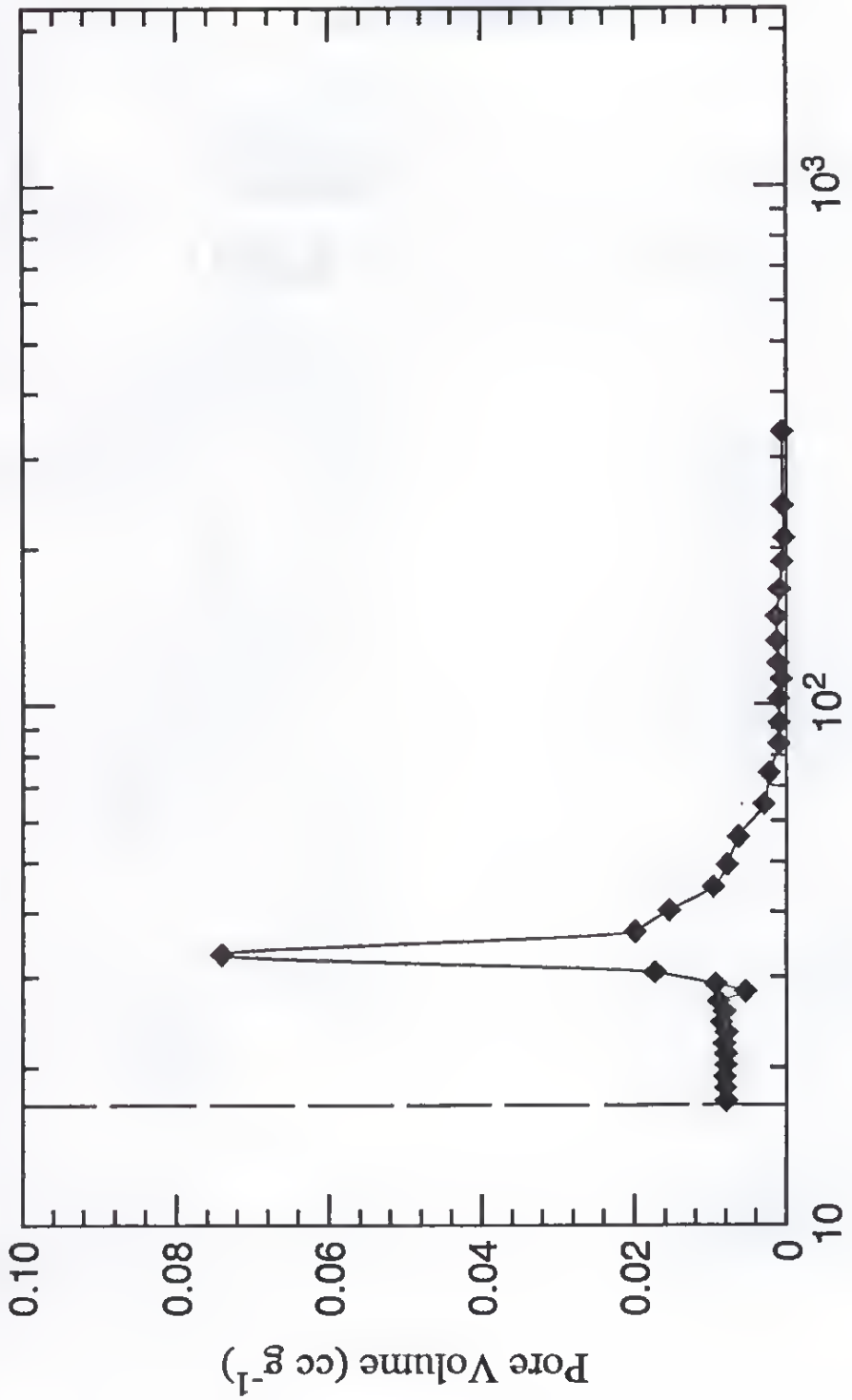

Figure 4-5: Pore Size Distribution for Fisher Silica Gel. The dashed line represents 17Å.

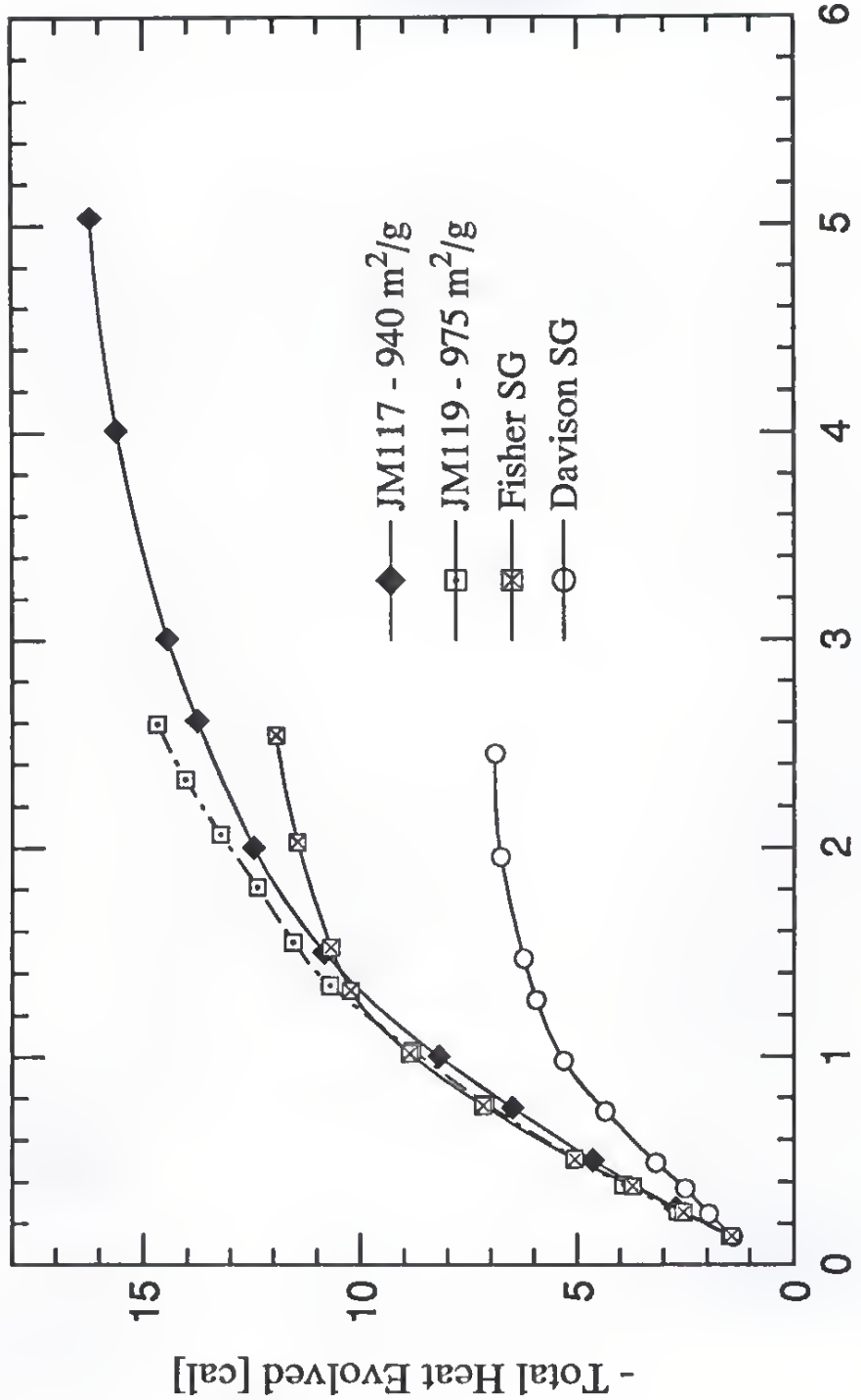

Figure 4-6: Calorimetric Titration of Commercial and Sol-Gel Silicas. The calorimetric curve represents the total heat evolved as a function of base added.

forming SO_4^{2-} on the surface of the solid. Sulfur trioxide is capable of functioning as a Lewis acid.[81,82] When SO_3 vapours are exposed to silica the SO_3 reacts quickly with the available hydroxyl sites to form -Si-O-S(O)$_2$OH which is a much stronger acid than silica alone. By controlling the surface area and the density of the hydroxyl sites on the solid as described above a large number of these strong sulfonated acid sites can be obtained. Figure 4-10 shows the difference between standard and SO_3 treated Davison and sol-gel silica JM119 with pyridine titration. The sol-gel silica experiences a greater total heat evolved as pyridine is added as a result of more acid sites being available on the surface compared to the Davison silica gel. The Davison silica has reached a plateau at roughly 2.5 mmoles of pyridine added, whereas the sol-gel sample has not reached its saturation point and can complex more base. The heat of interaction for the strongest acid site of a sulfated silica prepared in this manner was on the order of 28-30 kcal mole^{-1} for both solids.

However, as Kob[59] and Drago observed, surface coated sulfated silicas have a tendency for the sulfate group to be lost by hydrolysis on prolonged exposure to moisture. Incorporation of the sulfate group into the structure of the silica was accomplished by including diethyl sulfate, $SO_2(OEt)_2$ in a 1:1 mole ratio of TEOS to sulfate in the synthesis of a standard silica sol-gel. These reactions were performed in a teflon lined autoclave for a period of three days, after which time the solid obtained was crushed, followed by calcination in air at 400°C for twelve hours. TGA analysis of J2M199 and J2M253 indicated that calcination in air up to 400°C was sufficient for the removal of residual organic compounds as well as the removal of excess water and sulfuric acid, Figure 4-11.

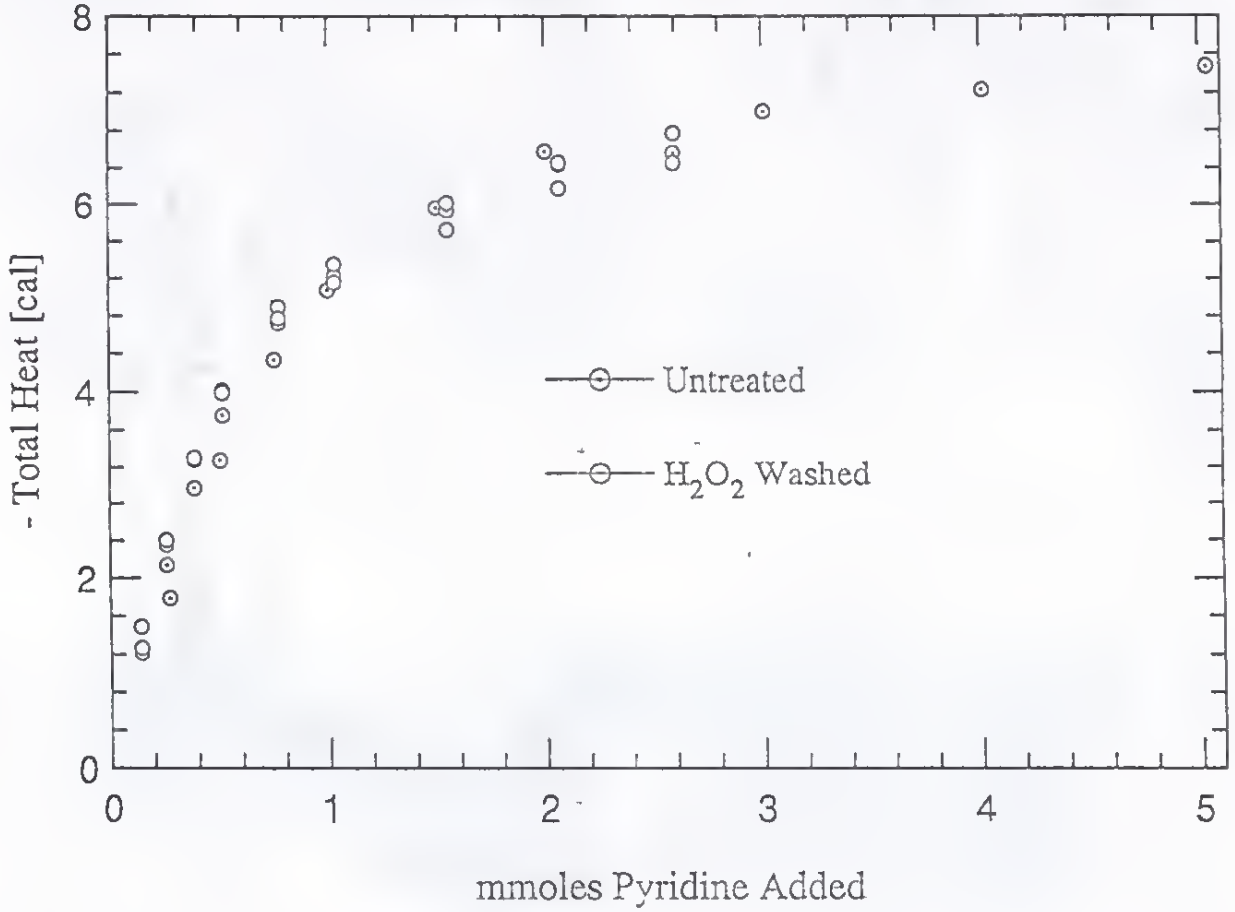

Figure 4-7: Effect of Peroxide Washing on Commercial Davison Silica Gel. The peroxide wash resulted in little change from the starting material.

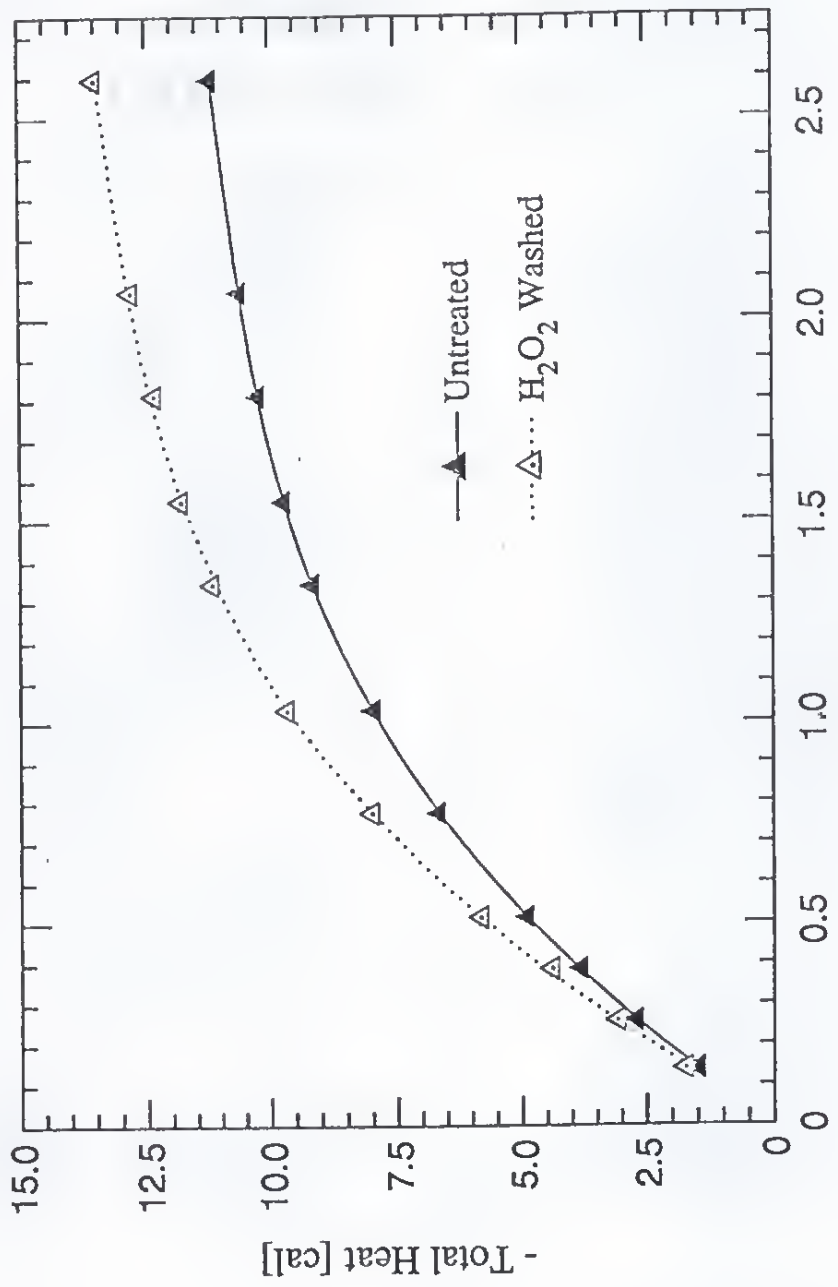

Figure 4-8: Effect of Peroxide Washing on Fisher Silica Gel.

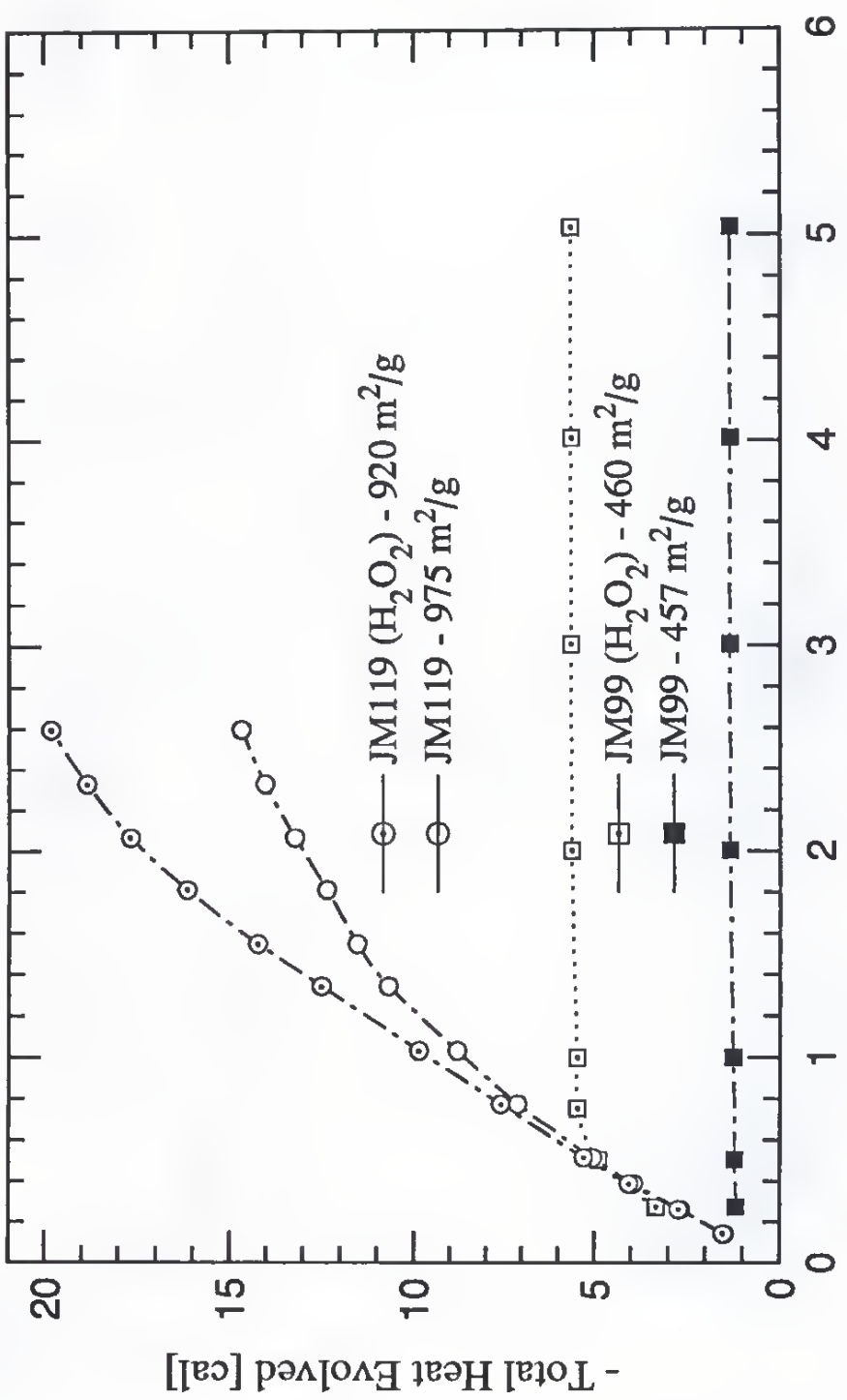

Figure 4-9: Effect of Peroxide Washing on Sol-Gel Derived Silicas.

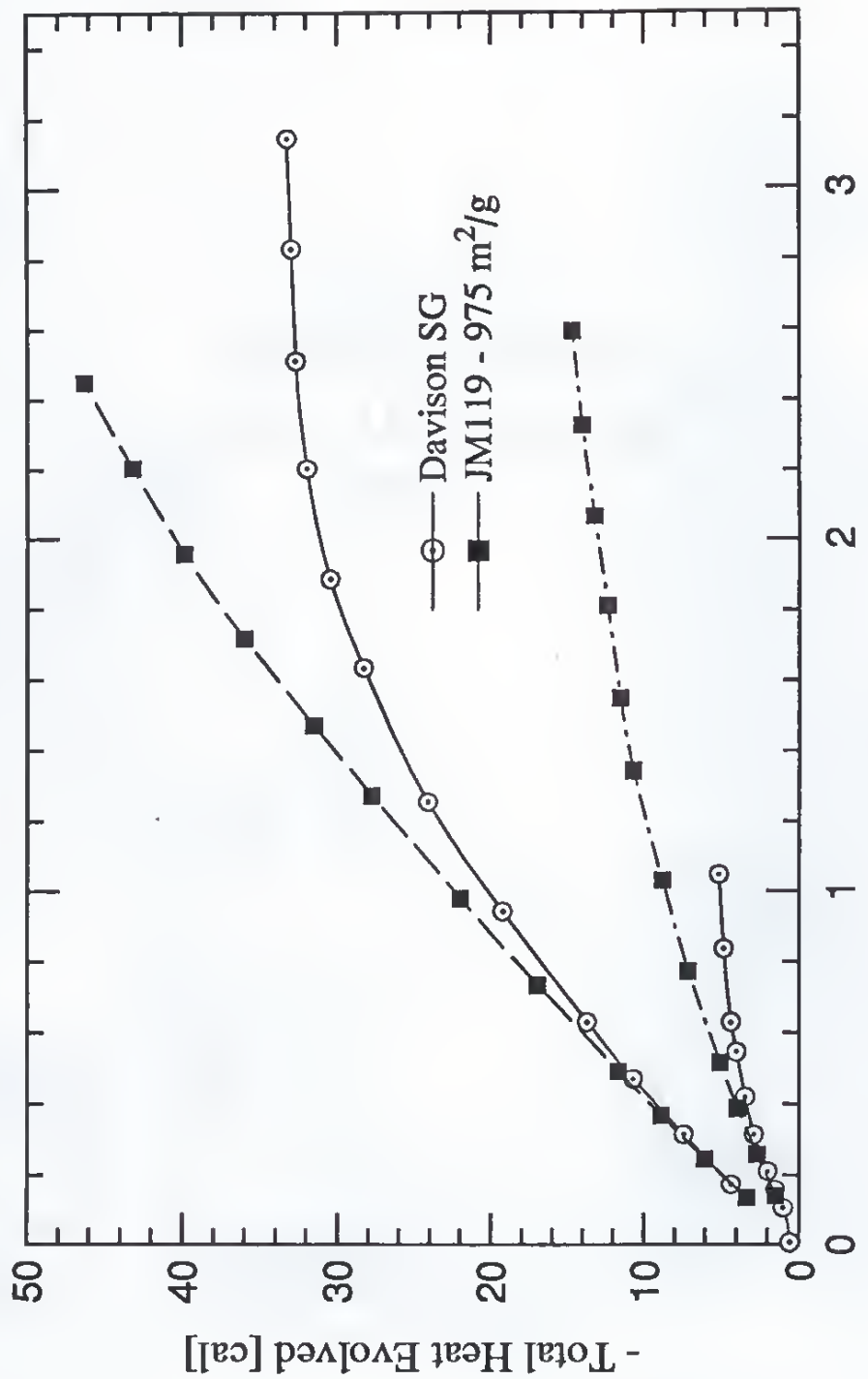

Figure 4-10: Calorimetric Titration of Standard and SO_3 Coated Silicas.

Infrared analysis indicated a peak at 1057 cm^{-1} which is reported to correspond to a bidentate bridging sulfate complex.[81,83] No peaks in the region corresponding to monodentate sulfate were observed. Table 4-2 lists the N_2 porosimetry and C, H, and N (carbon, hydrogen and nitrogen) data for the two 1:1 sulfate samples, as well as results for samples with 10% and 30% sulfate content after calcination in air at 400°C.

Table 4-2: N_2 Porosimetry and C, H, and N Results for Sulfated Silica Samples

Sample ID	Sulfate Content	BET Surface Area m^2g^{-1}	Total Pore Volume cc g^{-1}	Micropore Volume cc g^{-1}	Average Pore Diameter Å	C, H, and N %
J2M199	1:1	585	0.81	0	55	0.2, 4, 0
J2M253	1:1	580	0.79	0	52	0.15, 5, 0
J2M189	10%	460	0.23	0.06	20	0, 0.8, 0
J2M191	30%	482	0.41	0	34	0, 0.2, 0
J2M205	30%	450	0.32	0	29	0, 0.1, 0

The samples listed in Table 4-2 indicate reproducible surface areas and pore diameters for the corresponding silica / sulfate ratios. The samples with lower sulfate content had lower surface areas and pore diameters than the 1:1 samples.

The calorimetric titration of samples J2M199 and J2M253 produced in the manner described above resulted in heats of interaction corresponding to 28 kcal $mole^{-1}$ with pyridine for the strongest acid sites. Table 4-3 shows the results for a Cal-Ad analysis of J2M253 with pyridine where n_1 is the number of strong acid sites, K_1 is the equilibrium constant for binding to the strong site, and $-\Delta H_1$ is the enthalpy of interaction of the strongest site with pyridine.

Table 4-3: Cal-Ad Results for J2M253 Sol-Gel Derived Sulfated Silica

$n_1 = 0.3$ moles gram^{-1}	$n_2 = 0.7$ moles gram^{-1}
$K_1 = 14649$	$K_2 = 1106$
$-\Delta H_1 = 28.5$ kcal mole^{-1}	$-\Delta H_2 = 14$ kcal mole^{-1}

Sulfated silicas produced with 10% and 30 % sulfate content did not contain as many strong acid sites after calcination as did the 1:1 samples. Calorimetric analysis of samples J2M189, J2M205 and J2M191 resulted in a lower total heat evolved and a weaker enthalpy of interaction for the strongest acid site, 23 kcal mole^{-1}. Substitution of $SO_2(OEt)_2$ with H_2SO_4 produced a large number of acidic sites, however, calorimetric heats of only 23 kcal mole^{-1} were observed. Fellow colleague John Osegovic tested the sol-gel prepared sulfated silicas for their activity in the synthesis of MTBE, methyl t-butyl ether, an important anti-knock additive in gasoline. Current industrial synthesis of MTBE involves the alkylation of isobutene and methanol. However, current demands for MTBE are surpassing the supply of isobutene. An alternative approach to meeting the demand for MTBE is the direct synthesis from t-butanol and methanol. The reaction involves the dehydration of t-butanol to form a 3° carbocation, followed by attack by methanol. Loss of a proton results in MTBE, Figure 4-12. Gas phase reactions of t-butanol and methanol at 150°C using sulfated silicas of varying sulfate content and surface binding show that sol-gel derived samples with a 1:1 ratio of silicon to sulfate have acceptable activity for greater than 150 hours. Table 4-4 summarizes the preliminary results for the sulfated catalysts studied.

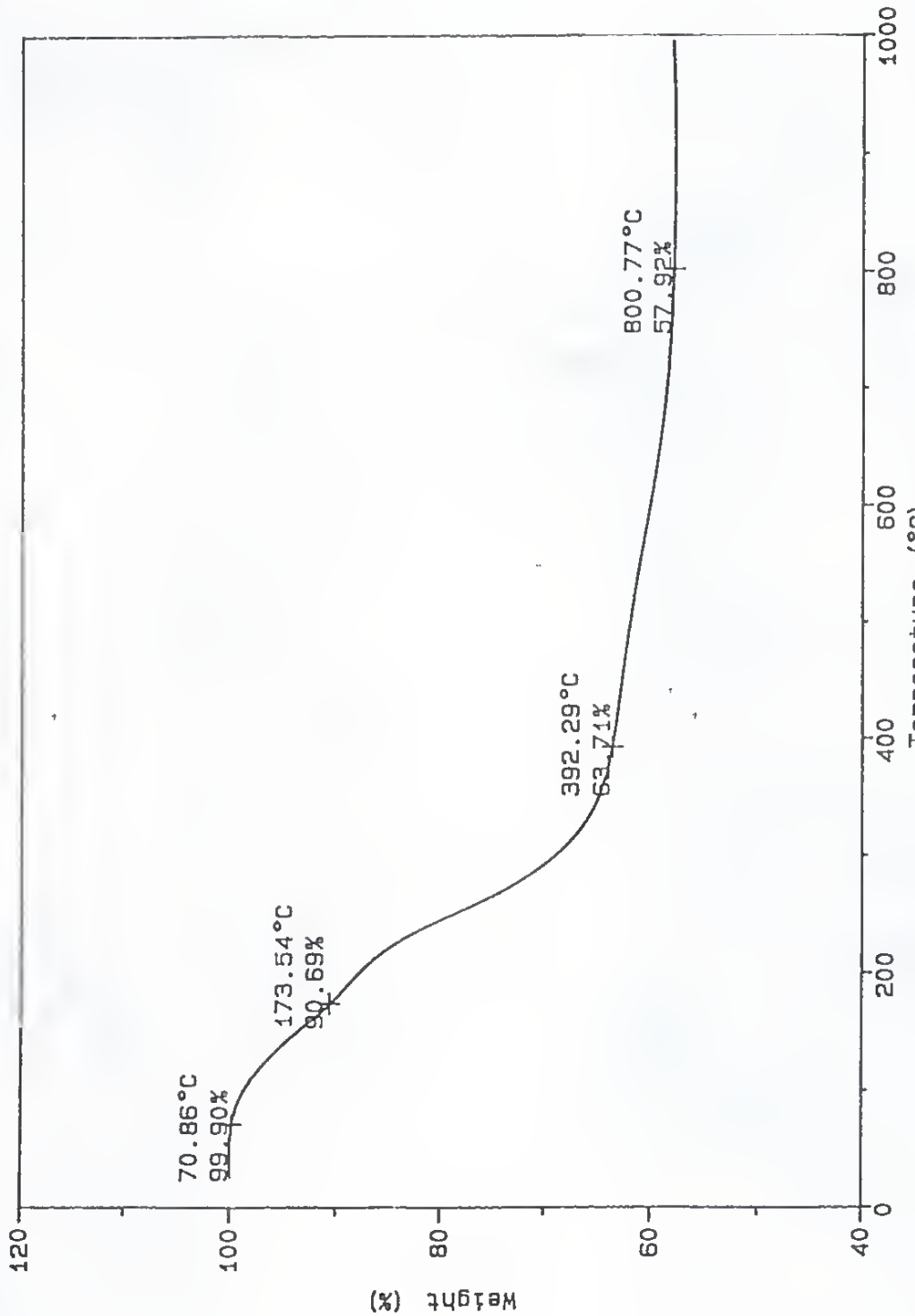

Figure 4-11: TGA Analysis of J2M199 Sulfated Sol-Gel Silica.

The lifetime of a catalyst is very important. Surface bound sulfated silicas prepared with aqueous washings of H_2SO_4 were able to sustain activity for approximately 30 hours before failing. Regeneration of the surface coated material involved removing the solid from the reactor and resulfating with aqueous washings of H_2SO_4. Regeneration by this method did not result in 100% activity being regained. Conversion of the reactants to MTBE was only reported to be 35%. Sulfated silicas of 10% and 30% synthesized by the sol-gel procedure revealed very short lifetimes for this reaction, with the 10% sample showing any activity. An ammonium sulfate derived sample, J2M187, which had the same silicon to sulfate ratio as J2M199 and J2M253, indicated good conversions to MTBE, however, it had a limited lifetime of 30-50 hours.

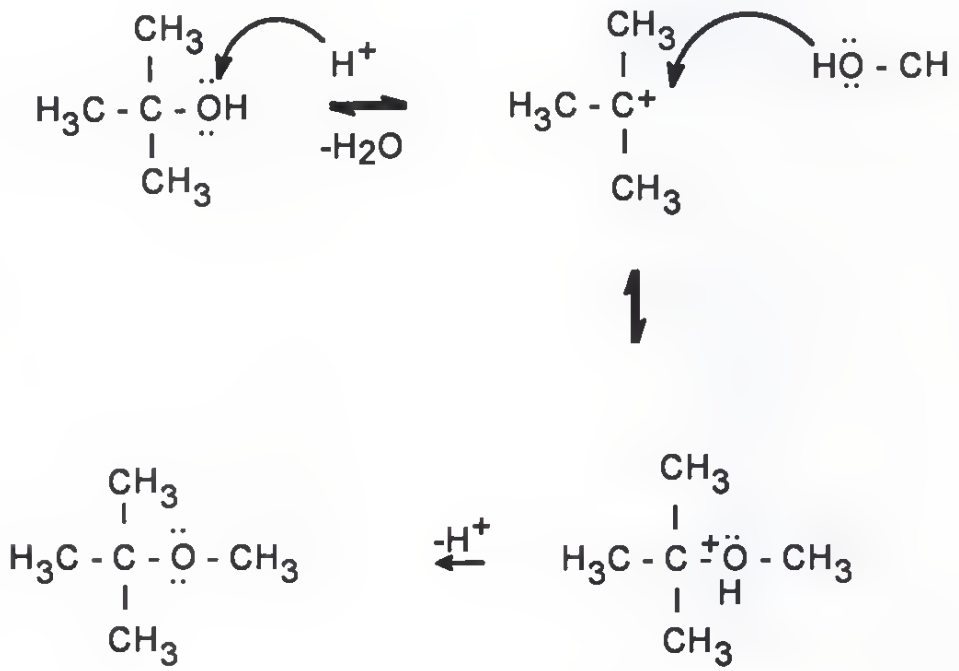

Figure 4-12: Acid Catalyzed Reaction of t-Butanol and Methanol to Produce MTBE

The 1:1 sulfated silica samples, J2M199 and J2M253, maintained catalytic activity beyond 150 hours with no indication of weakening after regeneration. Regeneration of the sample, when the activity dropped, was accomplished by simply stopping the flow of isobutanol and methanol for three hours while maintaining the flow of carrier gas, N_2, at 150°C. The activity of the solid returned to that of the starting material. One important step that was found to be critical to the activity of the solid was the degree of rehydration after calcination. Samples which were calcined and immediately used for MTBE synthesis had poor results, whereas those samples which were allowed to rehydrate for several hours prior to conditioning at 150°C in the gas phase flow reactor gave better results. Further studies of sol-gel derived silica sulfates are needed in order ascertain the potential for this catalyst to be used on an industrial scale.

Table 4-4: Preliminary Results for the Synthesis of MTBE from Sulfated Silica

Catalyst	Conversion of butanol %	% isobutene pruduced	MTBE / MIBE	% MTBE	Lifetime (hours)
Fisher SG Acid Washed	90	40	1.4	35	30
J2M189	93	0.2	---	73	14
J2M205	---	---	---	---	---
J2M253	94	22	22	89	150+
J2M187	100	10	---	90	30-50

Conclusions

The sol-gel method is a unique way of synthesizing silica and mixed metal silicates from the metal alkoxides. Incorporation of additives to control the porosity and reactivity of the solid is possible resulting in many potential applications. The ability to control the pore size and surface area of porous materials is important so that effective adsorption near catalytic sites can be achieved. With silica, high surface areas result in a large number of hydroxyl acid sites which are capable of undergoing exchange reactions. In the case of sulfated silicas, a large surface area results in a large number of strong acid sites generated when exposed to SO_3. However, surface coated silicas are susceptible to moisture which results in the loss of the active sulfate complex. By incorporating the sulfate complex into the silica framework, loss of strong acid sites was minimized. Sol-Gel sulfated silicas have exhibited thermal stability and repeated use in the synthesis of MTBE. Further work is necessary to optimize this solid and to assess the ability of sulfated silicas to be used on an industrial scale.

APPENDIX A

PRESSURE TABLE USED FOR COLLECTION OF ADSORPTION DATA

Pressure (torr)	Pressure (torr)
0.05	65.0
0.07	75.0
0.1	85.0
0.2	90.0
0.3	100.0
0.4	110.0
0.5	115.0
0.6	120.0
0.8	150.0
1.0	200.0
3.0	225.0
5.0	250.0
7.0	300.0
9.0	350.0
11.0	400.0
13.0	450.0
15.0	500.0
18.0	550.0
21.0	600.0
25.0	650.0
30.0	700.0
45.0	760.0
55.0	

APPENDIX B

GAS ADSORPTION DATA

A572 / CH_4
-43°C

pressure (atm)	moles. ads.
1.32553E-03	6.10601E-05
3.96776E-03	1.59869E-04
6.59566E-03	2.40430E-04
9.52171E-03	3.16682E-04
1.20393E-02	3.76278E-04
1.46251E-02	4.34492E-04
1.72109E-02	4.86571E-04
1.98647E-02	5.38913E-04
2.41516E-02	6.14014E-04
2.80303E-02	6.77889E-04
3.34739E-02	7.60007E-04
4.64026E-02	9.32127E-04
5.93995E-02	1.08074E-03
7.31447E-02	1.21957E-03
8.60054E-02	1.33520E-03
9.94105E-02	1.44420E-03
1.12679E-01	1.54371E-03
1.19144E-01	1.58786E-03
1.32209E-01	1.67507E-03
1.45138E-01	1.75634E-03
1.52282E-01	1.79772E-03
1.58815E-01	1.83505E-03
1.97601E-01	2.04268E-03
2.66123E-01	2.35248E-03
2.96744E-01	2.47113E-03
3.29134E-01	2.58825E-03
3.95683E-01	2.80504E-03
4.60735E-01	2.99279E-03
5.27012E-01	3.16354E-03
5.92744E-01	3.31589E-03
6.58137E-01	3.45464E-03
7.25162E-01	3.58437E-03
7.90758E-01	3.70090E-03
8.56491E-01	3.81015E-03
9.21203E-01	3.91078E-03
1.00163E+00	4.02659E-03

A572 / CH_4
0°C

pressure (atm)	moles ads.
1.35961E-03	9.11484E-06
3.94329E-03	2.63942E-05
6.63105E-03	4.36647E-05
9.69316E-03	6.26439E-05
1.18026E-02	7.55733E-05
1.50688E-02	9.54002E-05
1.71783E-02	1.07161E-04
1.96279E-02	1.20795E-04
2.38467E-02	1.44084E-04
2.84738E-02	1.68582E-04
3.37814E-02	1.94735E-04
4.60297E-02	2.53087E-04
5.95709E-02	3.13509E-04
7.24996E-02	3.67186E-04
8.55645E-02	4.18850E-04
9.89016E-02	4.68149E-04
1.12034E-01	5.14736E-04
1.18499E-01	5.36535E-04
1.31564E-01	5.80253E-04
1.45105E-01	6.23369E-04
1.51365E-01	6.43183E-04
1.58306E-01	6.63661E-04
1.98045E-01	7.78478E-04
2.65819E-01	9.50326E-04
2.96575E-01	1.02219E-03
3.28965E-01	1.09344E-03
3.95242E-01	1.22844E-03
4.60770E-01	1.35063E-03
5.26299E-01	1.46326E-03
5.92099E-01	1.56835E-03
6.58036E-01	1.66743E-03
7.23904E-01	1.75992E-03
7.89365E-01	1.84745E-03
8.55506E-01	1.93079E-03
9.21034E-01	2.00977E-03
1.00024E+00	2.10048E-03

A572 / CH_4 25°C		A572 / CH_4 40°C	
pressure (atm)	moles ads.	pressure (atm)	moles ads.
1.40316E-03	3.50674E-06	1.32763E-03	2.22629E-06
3.92961E-03	1.03016E-05	3.98276E-03	6.87517E-06
6.63987E-03	1.75738E-05	6.60658E-03	1.14527E-05
9.90618E-03	2.64834E-05	9.26039E-03	1.58026E-05
1.20836E-02	3.23459E-05	1.19142E-02	2.03846E-05
1.46013E-02	3.82573E-05	1.44318E-02	2.48416E-05
1.69829E-02	4.45302E-05	1.73579E-02	2.96823E-05
1.96367E-02	5.12671E-05	1.97395E-02	3.42420E-05
2.46041E-02	6.37459E-05	2.38903E-02	4.11618E-05
2.78703E-02	7.12457E-05	2.74967E-02	4.73365E-05
3.39264E-02	8.60712E-05	3.26683E-02	5.59026E-05
4.67191E-02	1.15584E-04	4.62775E-02	7.79780E-05
5.99200E-02	1.44731E-04	5.87299E-02	9.75685E-05
7.30529E-02	1.73392E-04	7.17947E-02	1.17958E-04
8.48249E-02	1.98537E-04	8.51317E-02	1.37905E-04
9.79578E-02	2.25060E-04	9.81966E-02	1.57103E-04
1.11159E-01	2.51379E-04	1.11329E-01	1.76153E-04
1.18644E-01	2.65785E-04	1.18814E-01	1.86919E-04
1.30892E-01	2.89208E-04	1.31335E-01	2.04229E-04
1.43821E-01	3.12907E-04	1.44332E-01	2.22022E-04
1.51578E-01	3.26854E-04	1.51545E-01	2.32074E-04
1.58247E-01	3.37709E-04	1.58349E-01	2.40488E-04
1.97373E-01	4.05840E-04	1.98224E-01	2.91514E-04
2.65691E-01	5.14638E-04	2.64433E-01	3.71165E-04
2.95631E-01	5.58977E-04	2.95870E-01	4.07286E-04
3.28974E-01	6.06161E-04	3.27988E-01	4.43103E-04
3.94843E-01	6.96391E-04	3.95286E-01	5.14067E-04
4.61528E-01	7.81016E-04	4.60610E-01	5.80137E-04
5.26308E-01	8.58526E-04	5.26887E-01	6.42161E-04
5.92108E-01	9.33479E-04	5.93300E-01	7.02677E-04
6.58249E-01	1.00435E-03	6.58011E-01	7.60828E-04
7.23777E-01	1.07110E-03	7.22519E-01	8.14138E-04
7.89578E-01	1.13544E-03	7.90837E-01	8.68908E-04
8.55787E-01	1.19523E-03	8.55617E-01	9.19416E-04
9.22472E-01	1.25171E-03	9.20329E-01	9.65401E-04
1.00059E+00	1.31918E-03	1.00096E+00	1.02518E-03

A572 / C_2H_6
25°C

pressure (atm)	moles ads.
9.73684E-05	3.44428E-06
1.42237E-04	7.02686E-06
2.71447E-04	2.75230E-05
4.03553E-04	4.24601E-05
5.42368E-04	6.27242E-05
6.58026E-04	7.48461E-05
7.93421E-04	9.02962E-05
1.07645E-03	1.17810E-04
1.31118E-03	1.40845E-04
4.13039E-03	3.37539E-04
6.53579E-03	4.65718E-04
9.46250E-03	5.22071E-04
1.18441E-02	6.03886E-04
1.46339E-02	7.04792E-04
1.72878E-02	7.84813E-04
1.96013E-02	8.50888E-04
2.40924E-02	9.59958E-04
2.74266E-02	1.03456E-03
3.29384E-02	1.14753E-03
3.94708E-02	1.26237E-03
5.95443E-02	1.55238E-03
7.18607E-02	1.69875E-03
8.47895E-02	1.83148E-03
9.81264E-02	1.95652E-03
1.12076E-01	2.07311E-03
1.17860E-01	2.11724E-03
1.31197E-01	2.21533E-03
1.45350E-01	2.31005E-03
1.50658E-01	2.34633E-03
1.58483E-01	2.39489E-03
1.97065E-01	2.60772E-03
2.62730E-01	2.90026E-03
2.96141E-01	3.03000E-03
3.28871E-01	3.14021E-03
3.93923E-01	3.33569E-03
4.61560E-01	3.50725E-03
5.25116E-01	3.64934E-03
5.91801E-01	3.78190E-03
6.57873E-01	3.89791E-03
7.23402E-01	4.00112E-03
7.89066E-01	4.09669E-03

A572 / C_2H_6
40°C

pressure (atm)	moles ads.
5.78947E-05	4.68903E-06
1.16316E-04	9.45391E-06
1.70789E-04	1.40136E-05
2.67368E-04	2.18613E-05
4.25263E-04	3.29258E-05
5.41711E-04	4.22950E-05
6.87895E-04	5.33015E-05
7.98816E-04	6.10199E-05
1.05000E-03	7.79379E-05
1.30921E-03	9.41956E-05
4.11000E-03	2.33162E-04
6.56368E-03	3.33060E-04
9.35355E-03	4.18805E-04
1.18033E-02	4.84898E-04
1.45251E-02	5.57121E-04
1.72470E-02	6.15878E-04
1.99688E-02	6.74070E-04
2.38474E-02	7.47323E-04
2.78621E-02	8.15624E-04
3.30337E-02	9.05412E-04
4.05187E-02	1.00736E-03
5.89592E-02	1.22850E-03
7.18199E-02	1.35474E-03
8.51570E-02	1.47945E-03
1.00195E-01	1.59109E-03
1.11355E-01	1.67574E-03
1.19044E-01	1.72818E-03
1.31360E-01	1.80796E-03
1.45106E-01	1.88926E-03
1.50821E-01	1.92394E-03
1.58579E-01	1.96516E-03
1.96480E-01	2.15236E-03
2.66704E-01	2.43313E-03
2.95487E-01	2.53347E-03
3.28626E-01	2.63677E-03
3.94834E-01	2.81921E-03
4.60635E-01	2.97744E-03
5.26163E-01	3.11553E-03
5.91420E-01	3.24174E-03
6.58581E-01	3.35489E-03
7.23157E-01	3.45267E-03

8.55139E-01	4.18679E-03
9.21688E-01	4.26774E-03
9.99464E-01	4.35534E-03

7.89366E-01	3.54370E-03
8.55370E-01	3.62558E-03
9.20967E-01	3.69982E-03

A572 / C_2H_6
55°C

pressure (atm)	moles ads.
1.04737E-04	4.47042E-06
2.09605E-04	8.69992E-06
3.23947E-04	1.24342E-05
4.13026E-04	1.58740E-05
5.55263E-04	2.12903E-05
6.70921E-04	2.55822E-05
8.15132E-04	3.09271E-05
1.07039E-03	3.98724E-05
1.31539E-03	4.83180E-05
4.06921E-03	1.29388E-04
6.54605E-03	1.90595E-04
9.47132E-03	2.52838E-04
1.17849E-02	2.97109E-04
1.45747E-02	3.46043E-04
1.73647E-02	3.92460E-04
2.01546E-02	4.34675E-04
2.39651E-02	4.87972E-04
2.75716E-02	5.37138E-04
3.32875E-02	6.05729E-04
3.94116E-02	6.71611E-04
5.93491E-02	8.61604E-04
7.22779E-02	9.64634E-04
8.50025E-02	1.05514E-03
9.83395E-02	1.14569E-03
1.12561E-01	1.23004E-03
1.17801E-01	1.25950E-03
1.31682E-01	1.33436E-03
1.45019E-01	1.40194E-03
1.51415E-01	1.43134E-03
1.57744E-01	1.46102E-03
1.97687E-01	1.63038E-03
2.65052E-01	1.86719E-03
2.95877E-01	1.96378E-03
3.29084E-01	2.05585E-03
3.94340E-01	2.21920E-03
4.60549E-01	2.36864E-03

A572 / C_2H_6
75°C

pressure (atm)	moles ads.
7.15789E-04	4.86842E-06
9.70395E-04	1.31579E-05
1.15408E-03	1.75000E-05
1.40724E-03	2.56579E-05
3.95553E-03	9.18553E-04
7.01487E-03	1.81368E-03
1.01450E-02	2.17947E-03
1.21183E-02	2.70250E-03
1.47721E-02	3.43303E-03
1.76300E-02	4.18224E-03
1.96034E-02	4.66605E-03
2.36182E-02	5.68132E-03
2.81772E-02	6.77671E-03
3.27363E-02	7.91855E-03
3.94729E-02	9.53000E-03
5.90021E-02	1.34605E-02
7.23391E-02	1.58349E-02
8.51997E-02	1.79608E-02
9.88089E-02	2.00550E-02
1.11874E-01	2.19345E-02
1.18474E-01	2.28001E-02
1.31403E-01	2.44391E-02
1.44876E-01	2.60755E-02
1.51409E-01	2.68217E-02
1.57941E-01	2.75691E-02
1.97476E-01	3.16066E-02
2.62324E-01	3.73989E-02
2.96143E-01	4.01192E-02
3.28941E-01	4.25050E-02
3.93653E-01	4.67546E-02
4.60338E-01	5.07388E-02
5.26342E-01	5.43029E-02
5.91803E-01	5.75633E-02
6.58011E-01	6.06021E-02
7.24152E-01	6.33293E-02
7.89000E-01	6.58183E-02

5.26894E-01	2.49787E-03
5.91061E-01	2.61367E-03
6.58427E-01	2.72221E-03
7.23070E-01	2.82055E-03
7.89892E-01	2.91371E-03
8.55624E-01	2.99489E-03
9.20608E-01	3.07113E-03
1.00022E+00	3.15825E-03
8.54733E-01	6.82988E-02
9.22234E-01	7.05921E-02
9.98922E-01	7.31505E-02
1.05275E+00	7.46921E-02
1.08575E+00	7.58213E-02

A572 / C_3H_8
100°C

pressure (atm)	moles ads.
3.50395E-04	2.81967E-06
6.11053E-04	4.95672E-06
7.96184E-04	6.47809E-06
1.05000E-03	8.59284E-06
1.40039E-03	1.14884E-05
3.98816E-03	3.20692E-05
6.61000E-03	5.16597E-05
9.94421E-03	7.40475E-05
1.25980E-02	9.17105E-05
1.45033E-02	1.04859E-04
1.81097E-02	1.26997E-04
1.98109E-02	1.37378E-04
2.43020E-02	1.65026E-04
2.77724E-02	1.82515E-04
3.37604E-02	2.14696E-04
4.01567E-02	2.46801E-04
5.90736E-02	3.32993E-04
7.17982E-02	3.88405E-04
8.56795E-02	4.39547E-04
9.92207E-02	4.89453E-04
1.12149E-01	5.35598E-04
1.18614E-01	5.57705E-04
1.30998E-01	5.94441E-04
1.45220E-01	6.39515E-04
1.52093E-01	6.59530E-04
1.58149E-01	6.75288E-04
1.98364E-01	7.81868E-04
2.65934E-01	9.38235E-04
2.96554E-01	1.00548E-03
3.29965E-01	1.06755E-03
3.94064E-01	1.18759E-03
4.63267E-01	1.29536E-03

A572 / C_3H_8
25°C

pressure (atm)	moles ads.
1.28197E-03	9.51762E-04
3.83513E-03	1.46998E-03
6.43645E-03	1.75443E-03
9.02224E-03	1.95336E-03
1.17441E-02	2.11517E-03
1.40576E-02	2.23357E-03
1.70517E-02	2.36485E-03
1.95013E-02	2.45778E-03
2.33800E-02	2.58605E-03
2.75308E-02	2.70751E-03
3.29064E-02	2.83800E-03
4.46784E-02	3.06668E-03
5.95124E-02	3.27829E-03
7.05359E-02	3.40199E-03
8.44172E-02	3.52912E-03
9.64614E-02	3.62351E-03
1.10343E-01	3.71252E-03
1.17147E-01	3.75554E-03
1.30076E-01	3.82597E-03
1.42665E-01	3.88792E-03
1.51375E-01	3.92615E-03
1.57703E-01	3.95375E-03
1.96829E-01	4.09021E-03
2.62630E-01	4.26959E-03
2.92910E-01	4.33582E-03
3.28226E-01	4.40231E-03
3.94503E-01	4.51061E-03
4.58739E-01	4.59416E-03
5.24879E-01	4.66993E-03
5.90476E-01	4.73621E-03
6.56957E-01	4.79303E-03
7.22893E-01	4.84275E-03

5.26550E-01	1.39498E-03
5.94664E-01	1.48309E-03
6.58355E-01	1.56814E-03
7.25857E-01	1.64432E-03
7.90364E-01	1.71701E-03
8.55553E-01	1.78964E-03
9.20877E-01	1.84760E-03
1.00015E+00	1.92503E-03
7.88286E-01	4.88981E-03
8.54358E-01	4.93232E-03
9.20499E-01	4.96948E-03
9.98616E-01	5.01247E-03

A572 / C_3H_8
40°C

pressure (atm)	moles ads.
1.28605E-03	6.39984E-04
3.84395E-03	1.06813E-03
6.40724E-03	1.31777E-03
9.12908E-03	1.45161E-03
1.16467E-02	1.59453E-03
1.41645E-02	1.71156E-03
1.68183E-02	1.82600E-03
1.96762E-02	1.92322E-03
2.31466E-02	2.04315E-03
2.81139E-02	2.17824E-03
3.21287E-02	2.28429E-03
4.78472E-02	2.58108E-03
5.75779E-02	2.71830E-03
7.04386E-02	2.87152E-03
8.52046E-02	3.02176E-03
9.75889E-02	3.12160E-03
1.10586E-01	3.21526E-03
1.18003E-01	3.26507E-03
1.30047E-01	3.33730E-03
1.43112E-01	3.39939E-03
1.49236E-01	3.43889E-03
1.58218E-01	3.47987E-03
1.97072E-01	3.63750E-03
2.67296E-01	3.84497E-03
2.92337E-01	3.91132E-03
3.30647E-01	3.98746E-03
3.94814E-01	4.10693E-03
4.59050E-01	4.20031E-03
5.24510E-01	4.28456E-03
5.90787E-01	4.35901E-03
6.56723E-01	4.42465E-03

A572 / C_3H_8
55°C

pressure (atm)	moles ads.
7.82895E-05	4.16525E-05
1.65395E-04	8.29258E-05
2.60000E-04	1.23807E-04
3.85132E-04	1.64522E-04
5.04211E-04	2.04354E-04
6.32763E-04	2.44062E-04
7.75789E-04	2.83220E-04
9.21316E-04	3.21308E-04
1.08605E-03	3.58664E-04
1.24803E-03	3.95373E-04
1.43645E-03	4.31248E-04
3.88000E-03	7.47734E-04
6.42079E-03	9.71197E-04
9.07461E-03	1.09399E-03
1.15243E-02	1.22119E-03
1.43822E-02	1.33355E-03
1.66278E-02	1.41826E-03
1.97579E-02	1.51728E-03
2.31601E-02	1.61796E-03
2.79914E-02	1.74061E-03
3.30949E-02	1.84532E-03
4.49349E-02	2.05783E-03
6.05175E-02	2.27027E-03
7.19492E-02	2.40356E-03
8.48779E-02	2.52953E-03
9.63778E-02	2.62911E-03
1.10191E-01	2.72300E-03
1.16655E-01	2.76757E-03
1.28836E-01	2.85153E-03
1.42921E-01	2.92637E-03
1.49590E-01	2.96326E-03

7.23000E-01	4.48190E-03
7.88733E-01	4.53208E-03
8.53989E-01	4.58259E-03
9.20266E-01	4.62783E-03
9.99063E-01	4.67597E-03

1.58096E-01	3.00598E-03
1.94500E-01	3.16620E-03
2.66765E-01	3.40199E-03
2.96637E-01	3.47636E-03
3.27190E-01	3.54644E-03
3.95032E-01	3.68807E-03
4.59539E-01	3.79055E-03
5.24047E-01	3.88060E-03
5.90664E-01	3.96148E-03
6.56601E-01	4.03291E-03
7.22674E-01	4.09683E-03
7.88610E-01	4.15435E-03
8.54547E-01	4.20668E-03
9.20619E-01	4.25317E-03
9.99145E-01	4.30382E-03

A572 / C_3H_8
75°C

pressure (atm)	moles ads.
1.53816E-04	4.11350E-05
3.34737E-04	8.14759E-05
5.64737E-04	1.20733E-04
7.94737E-04	1.59079E-04
1.04789E-03	1.96346E-04
1.31605E-03	2.32493E-04
3.87184E-03	4.67418E-04
6.39566E-03	6.30151E-04
9.11750E-03	7.35817E-04
1.16351E-02	8.37410E-04
1.42889E-02	9.31529E-04
1.73511E-02	1.01276E-03
1.93243E-02	1.07227E-03
2.44279E-02	1.18802E-03
2.68095E-02	1.24338E-03
3.44307E-02	1.37976E-03
4.57263E-02	1.55747E-03
6.03562E-02	1.73498E-03
7.13796E-02	1.83715E-03
8.51930E-02	1.97116E-03
9.81897E-02	2.06389E-03
1.09894E-01	2.14232E-03
1.18059E-01	2.19785E-03
1.29763E-01	2.26782E-03

A572 / C_3H_8
125°C

pressure (atm)	moles ads.
1.25921E-04	3.82350E-06
2.34737E-04	7.73177E-06
3.53816E-04	1.11582E-05
4.48421E-04	1.44642E-05
5.36842E-04	1.76095E-05
7.12500E-04	2.46275E-05
8.17237E-04	2.82993E-05
1.06895E-03	3.75390E-05
1.33579E-03	4.72249E-05
3.96987E-03	1.28148E-04
6.68276E-03	1.92924E-04
9.13250E-03	2.37080E-04
1.19904E-02	2.89114E-04
1.47122E-02	3.34148E-04
1.73661E-02	3.74355E-04
2.02239E-02	4.13786E-04
2.38984E-02	4.59262E-04
2.75729E-02	5.02628E-04
3.32208E-02	5.63233E-04
3.96171E-02	6.24543E-04
5.87380E-02	7.78112E-04
7.26875E-02	8.72767E-04
8.50718E-02	9.47006E-04
9.89533E-02	1.01918E-03

1.42011E-01	2.33680E-03
1.50585E-01	2.38462E-03
1.58002E-01	2.42374E-03
1.95496E-01	2.58958E-03
2.64494E-01	2.82409E-03
2.98245E-01	2.91163E-03
3.26756E-01	2.98146E-03
3.95143E-01	3.13758E-03
4.59854E-01	3.24857E-03
5.23273E-01	3.34688E-03
5.90571E-01	3.43661E-03
6.56576E-01	3.51556E-03
7.22853E-01	3.58556E-03
7.88721E-01	3.64827E-03
8.54658E-01	3.70480E-03
9.20458E-01	3.75681E-03
9.99392E-01	3.81232E-03
1.11746E-01	1.08050E-03
1.18278E-01	1.11019E-03
1.31819E-01	1.16723E-03
1.44680E-01	1.21916E-03
1.51417E-01	1.24507E-03
1.57881E-01	1.27046E-03
1.98028E-01	1.39982E-03
2.64101E-01	1.57734E-03
2.96627E-01	1.65304E-03
3.29017E-01	1.71815E-03
3.96246E-01	1.84326E-03
4.61571E-01	1.94806E-03
5.28120E-01	2.04079E-03
5.93716E-01	2.12388E-03
6.59857E-01	2.19880E-03
7.23684E-01	2.26127E-03
7.91050E-01	2.32540E-03
8.56986E-01	2.38586E-03
9.22106E-01	2.43107E-03
1.00084E+00	2.49680E-03
1.05473E+00	2.52689E-03
1.08630E+00	2.56704E-03

A572 / C_3H_8
150°C

pressure (atm)	moles ads.
3.45000E-04	3.35505E-06
5.43026E-04	6.62978E-06
6.96842E-04	9.27099E-06
8.15921E-04	1.14214E-05
1.09684E-03	1.61506E-05
1.31803E-03	1.96306E-05
3.94671E-03	6.43259E-05
7.08289E-03	1.08276E-04
1.06213E-02	1.18132E-04
1.20503E-02	1.35130E-04
1.44318E-02	1.65174E-04
1.69496E-02	1.93754E-04
2.04200E-02	2.26809E-04
2.41625E-02	2.62760E-04
2.83133E-02	3.00830E-04
3.36889E-02	3.45257E-04
3.98130E-02	3.91046E-04
5.87979E-02	5.13032E-04

A572 / C_3H_8
175°C

pressure (atm)	moles ads.
3.28684E-04	2.41367E-06
5.98158E-04	4.69350E-06
7.91316E-04	6.25502E-06
1.14724E-03	9.10145E-06
1.35750E-03	1.08548E-05
3.93105E-03	3.42732E-05
6.57461E-03	5.63933E-05
9.16039E-03	7.31507E-05
1.23586E-02	9.65379E-05
1.45361E-02	1.11408E-04
1.70537E-02	1.28853E-04
2.04561E-02	1.49902E-04
2.43346E-02	1.72923E-04
2.84174E-02	1.95440E-04
3.35208E-02	2.23842E-04
4.00533E-02	2.55836E-04
5.91742E-02	3.40872E-04
7.21029E-02	3.92572E-04

7.22030E-02	5.85433E-04
8.51317E-02	6.48733E-04
9.78563E-02	7.05827E-04
1.10921E-01	7.59766E-04
1.18338E-01	7.89047E-04
1.30791E-01	8.35014E-04
1.43788E-01	8.79847E-04
1.51341E-01	9.04925E-04
1.57873E-01	9.28023E-04
1.96795E-01	1.03914E-03
2.63753E-01	1.20038E-03
2.96959E-01	1.26858E-03
3.28396E-01	1.32899E-03
3.95354E-01	1.44437E-03
4.59725E-01	1.54164E-03
5.26002E-01	1.63241E-03
5.92483E-01	1.71016E-03
6.56787E-01	1.78428E-03
7.24220E-01	1.85104E-03
7.90429E-01	1.91316E-03
8.55753E-01	1.96716E-03
9.22438E-01	2.02498E-03
1.00171E+00	2.07867E-03
1.05390E+00	2.15444E-03
1.08718E+00	2.18264E-03
8.57803E-02	4.41902E-04
9.80286E-02	4.81886E-04
1.12863E-01	5.27322E-04
1.18306E-01	5.44677E-04
1.31099E-01	5.81222E-04
1.46001E-01	6.21460E-04
1.51309E-01	6.35384E-04
1.57909E-01	6.53783E-04
1.98737E-01	7.44048E-04
2.62768E-01	8.70692E-04
2.95838E-01	9.25346E-04
3.30542E-01	9.82538E-04
3.95594E-01	1.08419E-03
4.61190E-01	1.16024E-03
5.27263E-01	1.24202E-03
5.92655E-01	1.30780E-03
6.59000E-01	1.37148E-03
7.26094E-01	1.43193E-03
7.92370E-01	1.48634E-03
8.57559E-01	1.53816E-03
9.21862E-01	1.58166E-03
1.00005E+00	1.64340E-03
1.05523E+00	1.66947E-03
1.08613E+00	1.72885E-03

A572 / SO_2
25°C

pressure (atm)	moles ads.
1.29355E-03	3.86883E-04
3.88605E-03	8.03699E-04
6.45684E-03	1.10077E-03
9.04263E-03	1.33248E-03
1.16284E-02	1.53705E-03
1.44863E-02	1.73056E-03
1.68679E-02	1.88569E-03
1.95897E-02	2.04443E-03
2.32642E-02	2.24412E-03
2.73470E-02	2.45671E-03
3.29268E-02	2.71943E-03
4.56514E-02	3.23688E-03
5.88524E-02	3.70381E-03
7.19853E-02	4.11610E-03

A572 / SO_2
40°C

pressure (atm)	moles ads.
1.30855E-03	2.22133E-04
3.92355E-03	4.88645E-04
6.53316E-03	6.91282E-04
9.25500E-03	8.43147E-04
1.17726E-02	9.84661E-04
1.47667E-02	1.13235E-03
1.70122E-02	1.23744E-03
1.98701E-02	1.36201E-03
2.36126E-02	1.51473E-03
2.78316E-02	1.66681E-03
3.28670E-02	1.84220E-03
4.71566E-02	2.27233E-03
5.87245E-02	2.57266E-03
7.17892E-02	2.87763E-03

8.55264E-02	4.47989E-03
9.77747E-02	4.78028E-03
1.12200E-01	5.09067E-03
1.17032E-01	5.19335E-03
1.32206E-01	5.49475E-03
1.42957E-01	5.68604E-03
1.50919E-01	5.81724E-03
1.57587E-01	5.92483E-03
1.99027E-01	6.48789E-03
2.64760E-01	7.18157E-03
2.96129E-01	7.44104E-03
3.26001E-01	7.66288E-03
3.93435E-01	8.08409E-03
4.60392E-01	8.42586E-03
5.22518E-01	8.69441E-03
5.91517E-01	8.94634E-03
6.54187E-01	9.13576E-03
7.24819E-01	9.33802E-03
7.86061E-01	9.49135E-03
8.53426E-01	9.62791E-03
9.17389E-01	9.74938E-03
9.99589E-01	9.89976E-03

8.54666E-02	3.16658E-03
9.83953E-02	3.41865E-03
1.11868E-01	3.65994E-03
1.17516E-01	3.75371E-03
1.31057E-01	3.97477E-03
1.45415E-01	4.19113E-03
1.50519E-01	4.26996E-03
1.58140E-01	4.37158E-03
1.96382E-01	4.85653E-03
2.62386E-01	5.53123E-03
2.94912E-01	5.80898E-03
3.26758E-01	6.06038E-03
3.92354E-01	6.49897E-03
4.59244E-01	6.88363E-03
5.26881E-01	7.20361E-03
5.90913E-01	7.47671E-03
6.58618E-01	7.72673E-03
7.22241E-01	7.93999E-03
7.89811E-01	8.14143E-03
8.54251E-01	8.32063E-03
9.22093E-01	8.48708E-03
9.99393E-01	8.65799E-03

A572 / SO_2
55°C

pressure (atm)	moles ads.
1.31197E-03	1.29459E-04
3.91737E-03	3.02896E-04
6.53855E-03	4.38543E-04
9.32842E-03	5.46498E-04
1.18462E-02	6.50879E-04
1.46361E-02	7.52650E-04
1.71537E-02	8.34403E-04
1.98075E-02	9.18422E-04
2.39583E-02	1.03911E-03
2.76328E-02	1.13983E-03
3.26683E-02	1.26723E-03
4.62775E-02	1.57730E-03
5.96825E-02	1.83791E-03
7.19308E-02	2.05979E-03
8.58122E-02	2.28781E-03
9.86729E-02	2.47823E-03
1.11466E-01	2.65756E-03

A572 / SO_2
75°C

pressure (atm)	moles ads.
1.30789E-03	6.45623E-05
3.92487E-03	1.61372E-04
6.52079E-03	2.41742E-04
9.17461E-03	2.99134E-04
1.18284E-02	3.63376E-04
1.44142E-02	4.23057E-04
1.70680E-02	4.80735E-04
1.97899E-02	5.36111E-04
2.35324E-02	6.07428E-04
2.78192E-02	6.84813E-04
3.29228E-02	7.71879E-04
4.59876E-02	9.64647E-04
5.87803E-02	1.13403E-03
7.21172E-02	1.29662E-03
8.55224E-02	1.44769E-03
9.87233E-02	1.58473E-03
1.11584E-01	1.71273E-03

1.18270E-01	2.74738E-03
1.31471E-01	2.91524E-03
1.45080E-01	3.07694E-03
1.51068E-01	3.14339E-03
1.57669E-01	3.21748E-03
1.97136E-01	3.62632E-03
2.62324E-01	4.20050E-03
2.94237E-01	4.45531E-03
3.29145E-01	4.70336E-03
3.93653E-01	5.12145E-03
4.62515E-01	5.49900E-03
5.23961E-01	5.79913E-03
5.90782E-01	6.10232E-03
6.59508E-01	6.37221E-03
7.22451E-01	6.59226E-03
7.88932E-01	6.80270E-03
8.55413E-01	6.99134E-03
9.20261E-01	7.16251E-03
9.99807E-01	7.35989E-03

1.18525E-01	1.77648E-03
1.31453E-01	1.88960E-03
1.44654E-01	2.00188E-03
1.51255E-01	2.05680E-03
1.57651E-01	2.11450E-03
1.99091E-01	2.42505E-03
2.60605E-01	2.82806E-03
2.96261E-01	3.04538E-03
3.28923E-01	3.22962E-03
3.93091E-01	3.55792E-03
4.60592E-01	3.86816E-03
5.24964E-01	4.14695E-03
5.93078E-01	4.41395E-03
6.57177E-01	4.64724E-03
7.23522E-01	4.87291E-03
7.90071E-01	5.07824E-03
8.54919E-01	5.26168E-03
9.19427E-01	5.44530E-03
1.00265E+00	5.65681E-03

PPAN / CH_4
-43°C

pressure (atm)	moles ads.
1.31053E-03	5.29758E-05
3.93579E-03	1.41456E-04
6.52079E-03	2.13295E-04
9.58355E-03	2.87227E-04
1.18972E-02	3.37869E-04
1.48232E-02	3.93870E-04
1.74770E-02	4.40435E-04
2.02668E-02	4.86718E-04
2.38053E-02	5.43442E-04
2.80921E-02	6.05586E-04
3.29914E-02	6.69532E-04
4.61243E-02	8.22923E-04
5.98016E-02	9.55273E-04
7.23901E-02	1.06447E-03
8.56591E-02	1.16690E-03
9.86559E-02	1.25777E-03
1.11925E-01	1.34162E-03
1.18253E-01	1.37931E-03
1.31794E-01	1.45583E-03

PPAN / CH_4
0°C

pressure (atm)	moles ads.
1.36092E-03	6.86624E-06
3.94868E-03	2.03043E-05
6.63316E-03	3.38494E-05
9.96737E-03	5.01249E-05
1.19407E-02	5.98599E-05
1.44584E-02	7.05586E-05
1.78608E-02	8.61872E-05
1.99021E-02	9.52797E-05
2.47334E-02	1.15749E-04
2.77954E-02	1.28848E-04
3.38516E-02	1.53538E-04
4.63039E-02	2.00812E-04
5.96411E-02	2.48403E-04
7.30461E-02	2.93540E-04
8.54986E-02	3.32248E-04
9.79509E-02	3.70545E-04
1.10880E-01	4.07598E-04
1.18637E-01	4.28116E-04
1.30749E-01	4.61448E-04

1.44995E-01	1.52572E-03
1.51460E-01	1.55773E-03
1.57992E-01	1.58943E-03
1.98003E-01	1.76619E-03
2.65028E-01	2.00979E-03
2.96398E-01	2.10822E-03
3.28584E-01	2.20105E-03
3.95269E-01	2.37308E-03
4.60865E-01	2.52093E-03
5.26189E-01	2.65081E-03
5.91854E-01	2.76884E-03
6.57926E-01	2.87622E-03
7.23727E-01	2.97299E-03
7.89391E-01	3.06252E-03
8.55464E-01	3.14554E-03
9.21197E-01	3.22232E-03
1.00013E+00	3.30800E-03

1.44086E-01	4.95449E-04
1.51367E-01	5.13996E-04
1.58172E-01	5.30940E-04
1.97638E-01	6.21955E-04
2.63847E-01	7.56955E-04
2.95421E-01	8.15356E-04
3.28967E-01	8.74199E-04
3.95312E-01	9.81587E-04
4.60909E-01	1.07761E-03
5.26369E-01	1.16563E-03
5.92238E-01	1.24765E-03
6.57970E-01	1.32417E-03
7.23838E-01	1.39584E-03
7.89707E-01	1.46317E-03
8.55644E-01	1.52629E-03
9.22329E-01	1.58775E-03
1.00038E+00	1.65588E-03

PPAN / CH_4
25°C

pressure (atm)	moles ads.
1.32487E-03	2.35121E-06
3.94263E-03	7.57116E-06
6.64263E-03	1.28447E-05
9.50053E-03	1.79397E-05
1.18822E-02	2.27313E-05
1.46041E-02	2.80004E-05
1.72579E-02	3.31668E-05
1.99116E-02	3.83421E-05
2.37903E-02	4.52307E-05
2.76689E-02	5.21326E-05
3.27043E-02	6.20773E-05
4.58372E-02	8.55760E-05
5.88339E-02	1.07817E-04
7.21711E-02	1.30499E-04
8.53720E-02	1.52316E-04
9.85729E-02	1.72655E-04
1.11434E-01	1.92875E-04
1.18783E-01	2.04323E-04
1.31575E-01	2.23012E-04
1.44572E-01	2.42701E-04
1.51921E-01	2.52244E-04

PPAN / CH_4
40°C

pressure (atm)	moles ads.
1.35618E-03	1.63291E-06
3.97118E-03	5.06380E-06
6.60526E-03	8.57500E-06
9.73539E-03	1.21665E-05
1.18447E-02	1.53074E-05
1.45666E-02	1.90060E-05
1.72884E-02	2.23387E-05
1.98062E-02	2.57384E-05
2.36847E-02	3.07933E-05
2.77675E-02	3.61471E-05
3.30071E-02	4.28661E-05
4.72967E-02	6.05202E-05
5.94089E-02	7.49487E-05
7.24058E-02	9.03676E-05
8.56067E-02	1.05336E-04
9.86716E-02	1.19706E-04
1.11804E-01	1.34211E-04
1.19085E-01	1.42215E-04
1.31810E-01	1.55751E-04
1.44739E-01	1.68877E-04
1.51543E-01	1.76541E-04

1.57977E-01	2.60752E-04
1.97716E-01	3.14437E-04
2.64061E-01	3.95918E-04
2.95702E-01	4.33202E-04
3.29521E-01	4.71393E-04
3.95254E-01	5.40082E-04
4.59761E-01	6.03828E-04
5.25630E-01	6.64830E-04
5.91362E-01	7.23378E-04
6.57231E-01	7.78955E-04
7.23168E-01	8.31462E-04
7.89172E-01	8.80423E-04
8.54837E-01	9.27835E-04
9.20909E-01	9.72954E-04
9.99503E-01	1.02303E-03

1.58280E-01	1.82970E-04
1.96182E-01	2.20679E-04
2.61982E-01	2.82431E-04
2.96073E-01	3.13166E-04
3.29144E-01	3.42612E-04
3.93855E-01	3.96524E-04
4.60268E-01	4.47756E-04
5.26205E-01	4.96690E-04
5.92142E-01	5.43459E-04
6.57942E-01	5.87887E-04
7.23879E-01	6.28955E-04
7.89203E-01	6.70866E-04
8.55412E-01	7.10507E-04
9.21144E-01	7.48394E-04
1.00021E+00	7.91108E-04

PPAN / C_3H_8
125°C

pressure (atm)	moles ads.
1.85132E-04	5.34041E-06
4.00132E-04	1.08637E-05
5.49079E-04	1.49772E-05
7.58684E-04	2.06790E-05
8.43816E-04	2.29009E-05
1.05816E-03	2.85402E-05
1.32211E-03	3.53395E-05
4.03105E-03	9.65691E-05
6.68618E-03	1.44566E-04
9.95237E-03	1.94329E-04
1.24021E-02	2.27376E-04
1.44434E-02	2.52900E-04
1.78458E-02	2.90439E-04
1.96150E-02	3.09976E-04
2.43101E-02	3.55613E-04
2.75083E-02	3.85210E-04
3.39726E-02	4.37856E-04
4.08453E-02	4.88030E-04
6.03064E-02	6.06442E-04
7.31672E-02	6.71955E-04
8.53475E-02	7.27719E-04
9.82762E-02	7.78732E-04
1.11001E-01	8.27233E-04
1.18690E-01	8.53614E-04

PPAN / C_3H_8
150°C

pressure (atm)	moles ads.
3.81053E-04	3.48889E-06
6.59342E-04	6.30856E-06
8.32237E-04	7.96823E-06
1.06566E-03	1.04176E-05
1.31395E-03	1.33979E-05
3.95276E-03	4.66985E-05
6.68684E-03	7.71482E-05
1.01572E-02	1.10868E-04
1.23347E-02	1.31860E-04
1.48524E-02	1.52333E-04
1.78464E-02	1.78223E-04
2.00239E-02	1.93174E-04
2.43788E-02	2.24266E-04
2.76451E-02	2.47890E-04
3.40414E-02	2.86790E-04
4.05738E-02	3.27179E-04
6.01030E-02	4.19568E-04
7.26916E-02	4.75984E-04
8.60286E-02	5.26702E-04
9.80047E-02	5.72629E-04
1.11818E-01	6.12978E-04
1.19439E-01	6.35821E-04
1.30939E-01	6.76684E-04
1.45501E-01	7.07268E-04

1.31143E-01	8.95293E-04
1.44275E-01	9.35125E-04
1.51352E-01	9.55724E-04
1.58225E-01	9.73811E-04
1.97147E-01	1.07061E-03
2.65465E-01	1.20737E-03
2.95542E-01	1.25853E-03
3.28748E-01	1.30993E-03
3.94072E-01	1.39671E-03
4.60417E-01	1.47354E-03
5.26490E-01	1.53922E-03
5.93856E-01	1.59856E-03
6.60133E-01	1.65064E-03
7.26341E-01	1.69759E-03
7.92618E-01	1.73926E-03
8.58895E-01	1.77593E-03
9.24764E-01	1.81050E-03
1.00458E+00	1.84819E-03
1.05630E+00	1.87049E-03
1.08651E+00	1.90238E-03
1.51285E-01	7.30057E-04
1.58838E-01	7.42349E-04
1.98713E-01	8.31520E-04
2.65398E-01	9.63518E-04
2.96631E-01	1.00556E-03
3.28204E-01	1.05935E-03
3.94822E-01	1.13978E-03
4.60758E-01	1.21380E-03
5.25946E-01	1.28753E-03
5.94128E-01	1.33874E-03
6.60405E-01	1.39019E-03
7.25253E-01	1.44875E-03
7.93503E-01	1.48364E-03
8.58760E-01	1.52128E-03
9.24492E-01	1.55907E-03
1.00397E+00	1.60352E-03

PPAN / C_3H_8
175°C

pressure (atm)	moles ads.
4.65395E-04	2.57428E-06
7.99605E-04	4.47934E-06
1.14592E-03	6.50040E-06
1.34329E-03	7.62916E-06
3.92079E-03	2.33916E-05
6.71816E-03	3.93593E-05
9.16789E-03	5.21504E-05
1.17536E-02	6.56777E-05
1.44074E-02	7.89417E-05
1.70612E-02	9.09521E-05
1.96470E-02	1.02387E-04
2.47504E-02	1.23427E-04
2.77445E-02	1.35406E-04
3.27118E-02	1.54457E-04
3.91082E-02	1.78518E-04
5.97941E-02	2.46984E-04
7.22466E-02	2.83840E-04
8.56516E-02	3.19617E-04
9.84442E-02	3.52298E-04

PPAN / C_3H_8
25°C

pressure (atm)	moles ads.
1.31053E-03	8.14745E-04
3.92145E-03	1.22446E-03
6.52908E-03	1.44981E-03
9.31895E-03	1.60765E-03
1.19728E-02	1.72401E-03
1.45584E-02	1.81373E-03
1.69400E-02	1.88595E-03
1.97300E-02	1.95909E-03
2.36766E-02	2.04782E-03
2.76233E-02	2.12399E-03
3.30670E-02	2.21052E-03
4.60638E-02	2.36639E-03
5.89245E-02	2.48084E-03
7.16491E-02	2.56816E-03
8.48500E-02	2.64143E-03
9.79149E-02	2.70339E-03
1.11456E-01	2.75710E-03
1.17988E-01	2.78239E-03
1.31189E-01	2.82444E-03

1.11849E-01	3.83426E-04
1.18382E-01	3.99010E-04
1.31651E-01	4.27318E-04
1.44716E-01	4.53476E-04
1.51384E-01	4.66945E-04
1.58189E-01	4.80579E-04
1.96158E-01	5.46199E-04
2.62639E-01	6.45739E-04
2.97207E-01	6.90533E-04
3.30345E-01	7.31583E-04
3.95669E-01	8.01682E-04
4.63171E-01	8.67846E-04
5.29516E-01	9.25497E-04
5.95997E-01	9.76769E-04
6.62206E-01	1.02523E-03
7.28210E-01	1.06747E-03
7.94351E-01	1.10665E-03
8.60288E-01	1.14370E-03
9.26361E-01	1.17733E-03
1.00638E+00	1.21487E-03
1.43914E-01	2.86153E-03
1.51331E-01	2.88226E-03
1.58204E-01	2.90008E-03
1.98011E-01	2.98385E-03
2.63947E-01	3.08571E-03
2.97018E-01	3.12768E-03
3.28999E-01	3.16218E-03
3.93575E-01	3.22056E-03
4.60396E-01	3.26951E-03
5.26061E-01	3.31125E-03
5.92201E-01	3.34780E-03
6.58002E-01	3.37992E-03
7.23939E-01	3.40727E-03
7.91100E-01	3.43306E-03
8.57037E-01	3.45500E-03
9.22837E-01	3.47712E-03
1.00238E+00	3.49861E-03

PPAN / C_3H_8
40°C

pressure (atm)	moles ads.
1.31053E-03	5.42549E-04
3.91474E-03	8.86638E-04
6.52829E-03	1.08282E-03
9.31829E-03	1.22482E-03
1.19039E-02	1.32954E-03
1.44897E-02	1.41624E-03
1.70074E-02	1.48873E-03
1.97292E-02	1.55721E-03
2.36759E-02	1.64282E-03
2.75546E-02	1.71776E-03
3.34746E-02	1.81138E-03
4.57909E-02	1.96270E-03
5.88558E-02	2.08691E-03
7.16484E-02	2.18012E-03
8.47813E-02	2.26307E-03
9.79822E-02	2.32986E-03
1.10979E-01	2.38655E-03
1.18124E-01	2.41715E-03
1.30985E-01	2.46312E-03

PPAN / C_3H_8
55°C

pressure (atm)	moles ads.
1.30645E-03	3.70452E-04
3.93039E-03	6.55590E-04
6.55013E-03	8.24257E-04
9.54408E-03	9.56304E-04
1.20618E-02	1.05030E-03
1.43754E-02	1.12246E-03
1.70292E-02	1.19299E-03
1.98191E-02	1.25979E-03
2.40379E-02	1.34571E-03
2.77125E-02	1.41247E-03
3.31562E-02	1.49710E-03
4.61529E-02	1.65640E-03
5.90137E-02	1.78357E-03
7.22146E-02	1.88012E-03
8.55516E-02	1.96639E-03
9.80039E-02	2.03589E-03
1.11409E-01	2.09757E-03
1.17737E-01	2.12657E-03
1.30666E-01	2.18068E-03

1.43641E-01	2.50534E-03
1.51466E-01	2.52958E-03
1.58067E-01	2.54932E-03
1.97534E-01	2.64286E-03
2.63334E-01	2.75868E-03
2.96745E-01	2.80682E-03
3.28794E-01	2.84664E-03
3.95344E-01	2.91377E-03
4.59307E-01	2.96751E-03
5.25788E-01	3.01358E-03
5.91452E-01	3.05327E-03
6.57321E-01	3.08884E-03
7.23258E-01	3.11918E-03
7.88922E-01	3.14678E-03
8.54926E-01	3.17013E-03
9.20523E-01	3.19306E-03
9.99388E-01	3.21607E-03

1.44275E-01	2.22511E-03
1.50399E-01	2.24733E-03
1.58157E-01	2.27428E-03
1.97555E-01	2.37986E-03
2.62744E-01	2.51002E-03
2.96698E-01	2.56554E-03
3.29156E-01	2.60781E-03
3.95978E-01	2.68676E-03
4.60621E-01	2.74900E-03
5.26014E-01	2.80238E-03
5.92018E-01	2.84919E-03
6.58023E-01	2.88956E-03
7.25525E-01	2.92547E-03
7.91461E-01	2.95855E-03
8.57874E-01	2.98558E-03
9.23471E-01	3.01418E-03
1.00383E+00	3.03776E-03

PPAN / SO_2
75°C

pressure (atm)	moles ads.
1.32684E-03	2.07205E-04
3.95895E-03	4.09882E-04
6.61276E-03	5.38413E-04
9.40197E-03	6.42995E-04
1.18516E-02	7.18506E-04
1.44374E-02	7.83225E-04
1.70912E-02	8.44503E-04
1.96768E-02	9.03565E-04
2.40318E-02	9.83573E-04
2.78424E-02	1.04594E-03
3.31500E-02	1.11971E-03
4.57386E-02	1.26085E-03
5.90755E-02	1.37961E-03
7.27528E-02	1.48179E-03
8.52733E-02	1.55496E-03
9.86783E-02	1.63664E-03
1.11879E-01	1.69195E-03
1.18888E-01	1.72542E-03
1.31068E-01	1.77167E-03
1.45698E-01	1.82522E-03
1.51142E-01	1.84790E-03

PPAN / SO_2
25°C

pressure (atm)	moles ads.
1.30921E-03	1.07005E-03
3.92421E-03	1.64282E-03
6.53724E-03	1.98087E-03
9.19092E-03	2.24018E-03
1.18447E-02	2.44847E-03
1.44986E-02	2.63273E-03
1.70163E-02	2.76643E-03
1.96701E-02	2.91342E-03
2.40250E-02	3.10514E-03
2.73593E-02	3.25089E-03
3.39597E-02	3.47189E-03
4.60039E-02	3.82144E-03
5.97492E-02	4.11413E-03
7.17253E-02	4.33445E-03
8.57428E-02	4.54868E-03
9.86036E-02	4.70597E-03
1.11532E-01	4.84661E-03
1.17588E-01	4.91281E-03
1.33171E-01	5.05558E-03
1.43514E-01	5.14442E-03
1.51748E-01	5.20435E-03

1.58559E-01	1.87445E-03
1.96869E-01	1.98331E-03
2.63214E-01	2.12524E-03
2.96216E-01	2.18261E-03
3.28946E-01	2.22925E-03
3.95836E-01	2.31845E-03
4.59527E-01	2.39076E-03
5.26348E-01	2.45056E-03
5.91128E-01	2.50546E-03
6.57881E-01	2.55008E-03
7.22593E-01	2.59464E-03
7.89958E-01	2.62729E-03
8.56984E-01	2.66022E-03
9.20675E-01	2.69150E-03
9.99880E-01	2.72399E-03

1.57191E-01	5.24637E-03
1.97543E-01	5.47471E-03
2.63139E-01	5.75878E-03
2.94984E-01	5.86837E-03
3.28599E-01	5.96015E-03
3.94876E-01	6.13145E-03
4.63534E-01	6.26943E-03
5.26681E-01	6.37677E-03
5.91121E-01	6.47775E-03
6.58554E-01	6.56964E-03
7.24355E-01	6.66322E-03
7.91584E-01	6.74474E-03
8.54799E-01	6.81556E-03
9.20872E-01	6.88592E-03
1.00144E+00	6.95563E-03

PPAN / SO_2
40°C

pressure (atm)	moles ads.
1.30789E-03	6.93379E-04
3.93171E-03	1.12868E-03
6.54605E-03	1.40031E-03
9.13184E-03	1.60833E-03
1.19217E-02	1.77689E-03
1.44393E-02	1.91320E-03
1.70251E-02	2.04429E-03
1.99511E-02	2.16714E-03
2.37617E-02	2.32390E-03
2.73682E-02	2.44556E-03
3.26757E-02	2.61888E-03
4.79180E-02	3.00321E-03
5.87374E-02	3.23493E-03
7.28909E-02	3.47308E-03
8.54114E-02	3.66374E-03
9.97011E-02	3.84093E-03
1.11473E-01	3.97105E-03
1.17325E-01	4.04210E-03
1.34132E-01	4.19847E-03
1.44271E-01	4.27817E-03
1.51144E-01	4.33985E-03
1.57404E-01	4.39420E-03
1.97211E-01	4.65244E-03
2.62535E-01	4.98673E-03

PPAN / SO_2
55°C

pressure (atm)	moles ads.
1.31118E-03	4.51820E-04
3.93171E-03	7.76608E-04
6.54263E-03	9.83707E-04
9.19711E-03	1.14434E-03
1.19189E-02	1.28331E-03
1.44367E-02	1.39626E-03
1.72266E-02	1.49597E-03
1.97442E-02	1.59309E-03
2.36909E-02	1.71295E-03
2.75014E-02	1.82800E-03
3.29451E-02	1.96920E-03
4.63503E-02	2.25748E-03
5.88707E-02	2.47952E-03
7.20036E-02	2.68865E-03
8.60211E-02	2.87808E-03
9.82693E-02	3.02157E-03
1.11606E-01	3.16131E-03
1.17390E-01	3.22625E-03
1.33994E-01	3.37971E-03
1.44609E-01	3.47358E-03
1.51890E-01	3.52647E-03
1.56789E-01	3.56975E-03
1.98909E-01	3.86042E-03
2.63281E-01	4.20381E-03

2.96014E-01	5.13293E-03
3.29425E-01	5.24962E-03
3.94409E-01	5.44748E-03
4.61638E-01	5.61233E-03
5.26486E-01	5.74490E-03
5.92354E-01	5.87601E-03
6.60264E-01	5.98661E-03
7.23207E-01	6.08589E-03
7.90573E-01	6.17954E-03
8.54740E-01	6.26165E-03
9.20336E-01	6.34588E-03
1.00267E+00	6.42938E-03

2.96419E-01	4.35008E-03
3.29694E-01	4.48278E-03
3.95495E-01	4.70845E-03
4.61091E-01	4.89185E-03
5.26007E-01	5.06172E-03
5.94801E-01	5.20440E-03
6.57064E-01	5.32871E-03
7.22524E-01	5.42962E-03
7.88733E-01	5.55325E-03
8.55350E-01	5.63965E-03
9.21627E-01	5.75011E-03
1.00519E+00	5.86234E-03

PPAN / SO_2
75°C

pressure (atm)	moles ads.
1.31053E-03	2.51816E-04
3.92487E-03	4.66985E-04
6.56171E-03	6.12613E-04
9.21553E-03	7.27831E-04
1.18692E-02	8.22789E-04
1.45911E-02	9.06955E-04
1.71088E-02	9.80918E-04
1.99667E-02	1.05758E-03
2.37774E-02	1.14815E-03
2.76559E-02	1.22853E-03
3.27595E-02	1.33041E-03
4.75254E-02	1.57124E-03
5.89571E-02	1.73312E-03
7.24983E-02	1.89605E-03
8.50868E-02	2.02947E-03
9.82197E-02	2.16053E-03
1.12577E-01	2.28490E-03
1.18225E-01	2.34151E-03
1.30746E-01	2.43789E-03
1.44151E-01	2.54508E-03
1.52725E-01	2.59451E-03
1.57420E-01	2.63310E-03
1.96886E-01	2.87668E-03
2.63231E-01	3.21372E-03
2.96506E-01	3.35232E-03
3.29032E-01	3.48133E-03
3.95377E-01	3.71046E-03

ZSM5 / CH_4
0°C

pressure (atm)	moles ads.
5.74342E-04	1.00384E-06
8.72368E-04	1.64183E-06
1.05263E-03	2.01660E-06
1.35408E-03	2.69921E-06
3.91474E-03	9.39145E-06
6.69092E-03	1.66771E-05
9.54816E-03	2.06255E-05
1.19979E-02	2.74070E-05
1.45155E-02	3.36129E-05
1.70333E-02	3.98144E-05
1.96191E-02	4.64754E-05
2.43822E-02	5.95342E-05
2.77166E-02	6.81360E-05
3.39087E-02	8.37735E-05
3.91483E-02	9.65290E-05
5.90178E-02	1.44138E-04
7.20825E-02	1.74650E-04
8.52834E-02	2.04426E-04
9.90288E-02	2.34148E-04
1.11005E-01	2.59396E-04
1.18626E-01	2.75194E-04
1.30466E-01	2.99317E-04
1.45028E-01	3.28130E-04
1.51424E-01	3.40604E-04
1.58093E-01	3.53266E-04
1.96471E-01	4.23173E-04
2.62611E-01	5.31538E-04

4.60089E-01	3.90705E-03
5.27182E-01	4.07591E-03
5.92710E-01	4.22582E-03
6.57422E-01	4.36582E-03
7.23563E-01	4.50398E-03
7.91677E-01	4.62130E-03
8.55436E-01	4.74585E-03
9.25592E-01	4.85800E-03
1.00146E+00	4.98368E-03

2.95274E-01	5.80597E-04
3.28956E-01	6.28304E-04
3.93668E-01	7.12126E-04
4.60762E-01	7.90787E-04
5.26494E-01	8.60087E-04
5.91954E-01	9.23704E-04
6.58095E-01	9.82301E-04
7.23624E-01	1.03570E-03
7.89628E-01	1.08490E-03
8.55156E-01	1.13048E-03
9.21229E-01	1.17306E-03
1.00009E+00	1.22013E-03

ZSM5 / CH_4
-16°C

pressure (atm)	moles ads.
3.38816E-04	1.36076E-06
5.64079E-04	2.39582E-06
7.28158E-04	3.14089E-06
8.64211E-04	3.76104E-06
1.08539E-03	4.78719E-06
1.31605E-03	5.87133E-06
3.96579E-03	1.83724E-05
6.58408E-03	3.05880E-05
9.57816E-03	4.42224E-05
1.24361E-02	5.66789E-05
1.43414E-02	6.57491E-05
1.76757E-02	8.07263E-05
1.97851E-02	8.95869E-05
2.35957E-02	1.06447E-04
2.80867E-02	1.25747E-04
3.30541E-02	1.46150E-04
3.97225E-02	1.73927E-04
6.02045E-02	2.53123E-04
7.20445E-02	2.96221E-04
8.51774E-02	3.41599E-04
9.87186E-02	3.86660E-04
1.12056E-01	4.28884E-04
1.18316E-01	4.48135E-04
1.31789E-01	4.87945E-04
1.44990E-01	5.24735E-04
1.51250E-01	5.41679E-04
1.57987E-01	5.59842E-04

ZSM5 / CH_4
-42°C

pressure (atm)	moles ads.
1.96711E-04	2.91336E-06
3.72237E-04	5.31364E-06
5.06316E-04	7.42393E-06
6.05658E-04	8.96761E-06
6.98816E-04	1.04087E-05
8.56711E-04	1.29517E-05
1.05197E-03	1.61060E-05
1.32079E-03	2.05586E-05
3.99776E-03	6.48568E-05
6.66987E-03	1.07018E-04
9.11947E-03	1.43718E-04
1.18413E-02	1.83002E-04
1.45632E-02	2.20434E-04
1.72170E-02	2.55969E-04
2.00068E-02	2.91153E-04
2.37495E-02	3.36629E-04
2.79683E-02	3.85786E-04
3.32079E-02	4.41755E-04
3.96722E-02	5.07076E-04
6.04943E-02	6.87891E-04
7.22663E-02	7.74105E-04
8.51270E-02	8.57022E-04
9.86001E-02	9.34791E-04
1.12005E-01	1.00345E-03
1.17993E-01	1.03185E-03
1.31671E-01	1.09196E-03
1.45008E-01	1.14474E-03

1.97045E-01	6.56790E-04
2.65023E-01	8.01138E-04
2.95372E-01	8.58053E-04
3.28646E-01	9.15133E-04
3.95331E-01	1.01660E-03
4.60860E-01	1.10306E-03
5.26048E-01	1.17818E-03
5.91712E-01	1.24553E-03
6.57921E-01	1.30569E-03
7.23517E-01	1.35924E-03
7.89386E-01	1.40797E-03
8.55323E-01	1.45210E-03
9.20987E-01	1.49246E-03
1.00006E+00	1.53697E-03

1.51132E-01	1.16697E-03
1.58004E-01	1.19076E-03
1.97675E-01	1.31614E-03
2.67150E-01	1.48273E-03
2.95661E-01	1.53652E-03
3.27779E-01	1.59069E-03
3.95553E-01	1.68735E-03
4.60809E-01	1.76238E-03
5.26814E-01	1.82603E-03
5.91866E-01	1.87914E-03
6.57734E-01	1.92576E-03
7.23671E-01	1.96665E-03
7.89472E-01	2.00253E-03
8.55204E-01	2.03490E-03
9.21141E-01	2.06400E-03
1.00014E+00	2.09494E-03

ZSM5 / CH_4
-84°C

pressure (atm)	moles ads.
2.59211E-05	2.45829E-06
4.48684E-05	4.81842E-06
5.71053E-05	7.16516E-06
7.14474E-05	9.48068E-06
1.02763E-04	1.61239E-05
1.42237E-04	2.46185E-05
2.70789E-04	5.20969E-05
3.94605E-04	7.29276E-05
5.31447E-04	9.89248E-05
6.58684E-04	1.21607E-04
7.86579E-04	1.43683E-04
1.05000E-03	1.86526E-04
1.30645E-03	2.25346E-04
4.00316E-03	5.48229E-04
6.59776E-03	7.60435E-04
9.18355E-03	9.17418E-04
1.19054E-02	1.05055E-03
1.43550E-02	1.15276E-03
1.69408E-02	1.24123E-03
1.96626E-02	1.32149E-03
2.36092E-02	1.42129E-03
2.75559E-02	1.50098E-03
3.26593E-02	1.59179E-03
3.98722E-02	1.69436E-03

ZSM5 / CO
0°C

pressure (atm)	moles ads.
5.43026E-04	4.55073E-07
8.73684E-04	7.62916E-07
1.10842E-03	9.68145E-07
1.42487E-03	1.25814E-06
3.98539E-03	4.18042E-06
6.70053E-03	7.29455E-06
9.96671E-03	1.09173E-05
1.18720E-02	1.33131E-05
1.44578E-02	1.62532E-05
1.78600E-02	1.97867E-05
1.97654E-02	2.20487E-05
2.47328E-02	2.72464E-05
2.75226E-02	3.04988E-05
3.39870E-02	3.76060E-05
3.92264E-02	4.31338E-05
5.92321E-02	6.42322E-05
7.21608E-02	7.74293E-05
8.52937E-02	9.04167E-05
9.90389E-02	1.03931E-04
1.11015E-01	1.15374E-04
1.18636E-01	1.22624E-04
1.30612E-01	1.33796E-04
1.43609E-01	1.45561E-04
1.51366E-01	1.52458E-04

6.06943E-02	1.89512E-03
7.20580E-02	1.97171E-03
8.53951E-02	2.04140E-03
9.80516E-02	2.09565E-03
1.11525E-01	2.14429E-03
1.17785E-01	2.16388E-03
1.31258E-01	2.20256E-03
1.45412E-01	2.23733E-03
1.50855E-01	2.24918E-03
1.57864E-01	2.26385E-03
1.97603E-01	2.33589E-03
2.66261E-01	2.42461E-03
2.95249E-01	2.45345E-03
3.27843E-01	2.48204E-03
3.95345E-01	2.53161E-03
4.60533E-01	2.57088E-03
5.25993E-01	2.60389E-03
5.91862E-01	2.63261E-03
6.57866E-01	2.65786E-03
7.23667E-01	2.68045E-03
7.89536E-01	2.70058E-03
8.55336E-01	2.71869E-03
9.21069E-01	2.73513E-03
1.00000E+00	2.75334E-03

1.58171E-01	1.58606E-04
1.97093E-01	1.92072E-04
2.63710E-01	2.45521E-04
2.95624E-01	2.69925E-04
3.29103E-01	2.94517E-04
3.94971E-01	3.40729E-04
4.60976E-01	3.83765E-04
5.26232E-01	4.24177E-04
5.92441E-01	4.63157E-04
6.58173E-01	4.99549E-04
7.23770E-01	5.34130E-04
7.89570E-01	5.67467E-04
8.55575E-01	5.99059E-04
9.21103E-01	6.29245E-04
1.00038E+00	6.63447E-04

ZSM5 / CO
-16°C

pressure (atm)	moles ads.
4.97368E-04	1.08414E-06
8.08421E-04	1.83368E-06
1.16158E-03	2.67244E-06
1.34934E-03	3.09628E-06
3.94053E-03	9.35130E-06
6.66105E-03	1.56822E-05
9.92724E-03	2.34006E-05
1.19687E-02	2.79111E-05
1.44183E-02	3.34925E-05
1.70041E-02	3.93593E-05
1.95897E-02	4.48068E-05
2.44891E-02	5.49344E-05
2.76872E-02	6.15820E-05
3.38795E-02	7.39225E-05

ZSM5 / CO
-43°C

pressure (atm)	moles ads.
2.70132E-04	2.37352E-06
5.10395E-04	4.19827E-06
6.61447E-04	5.44749E-06
8.07763E-04	6.61640E-06
1.09211E-03	8.88284E-06
1.35618E-03	1.09574E-05
3.96092E-03	3.09360E-05
6.58408E-03	4.98305E-05
9.78224E-03	7.11966E-05
1.24361E-02	8.88195E-05
1.45455E-02	1.01263E-04
1.74714E-02	1.19198E-04
1.97170E-02	1.31690E-04
2.39359E-02	1.55323E-04

3.91189E-02	8.44606E-05
5.92607E-02	1.22803E-04
7.21893E-02	1.46136E-04
8.55264E-02	1.69314E-04
9.78428E-02	1.90033E-04
1.10976E-01	2.11230E-04
1.18529E-01	2.23343E-04
1.30845E-01	2.42170E-04
1.43706E-01	2.61350E-04
1.51395E-01	2.72513E-04
1.58132E-01	2.82078E-04
1.97122E-01	3.35317E-04
2.64283E-01	4.17208E-04
2.95244E-01	4.51847E-04
3.28995E-01	4.88007E-04
3.95340E-01	5.53270E-04
4.60800E-01	6.11711E-04
5.26329E-01	6.65513E-04
5.92197E-01	7.15530E-04
6.57998E-01	7.62037E-04
7.23730E-01	8.05577E-04
7.89735E-01	8.46181E-04
8.55468E-01	8.83506E-04
9.21200E-01	9.19385E-04
1.00034E+00	9.59623E-04

ZSM5 / CO
-93°C

pressure (atm)	moles ads.
1.09211E-05	2.38244E-06
2.03947E-05	5.01026E-06
2.85526E-05	7.42393E-06
3.60526E-05	9.82868E-06
4.35526E-05	1.22156E-05
5.03947E-05	1.45936E-05
5.78947E-05	1.69582E-05
6.46053E-05	1.93049E-05
7.27632E-05	2.16338E-05
1.00658E-04	3.04809E-05
1.38816E-04	4.15187E-05
2.64737E-04	7.54528E-05
3.93947E-04	1.02775E-04

2.84270E-02	1.79473E-04
3.36664E-02	2.05992E-04
3.95864E-02	2.34434E-04
5.97282E-02	3.21777E-04
7.21805E-02	3.69608E-04
8.53814E-02	4.16267E-04
9.89226E-02	4.60190E-04
1.11919E-01	4.98898E-04
1.18316E-01	5.16793E-04
1.31721E-01	5.52976E-04
1.43425E-01	5.83095E-04
1.51522E-01	6.02507E-04
1.57851E-01	6.17444E-04
1.96637E-01	7.02855E-04
2.65227E-01	8.28995E-04
2.96528E-01	8.78116E-04
3.28578E-01	9.24422E-04
3.95127E-01	1.01069E-03
4.60996E-01	1.08406E-03
5.25980E-01	1.14808E-03
5.92052E-01	1.20633E-03
6.57989E-01	1.25807E-03
7.23585E-01	1.30496E-03
7.89590E-01	1.34785E-03
8.55254E-01	1.38729E-03
9.21191E-01	1.42350E-03
1.00012E+00	1.46326E-03

ZSM5 / N_2
-93°C

pressure (atm)	moles ads.
1.68816E-04	3.10966E-06
3.21842E-04	8.78915E-06
4.45658E-04	1.39600E-05
5.58684E-04	1.86401E-05
6.87895E-04	2.44044E-05
8.09079E-04	2.92630E-05
1.07171E-03	3.98322E-05
1.33237E-03	4.95940E-05
3.92697E-03	1.44776E-04
6.53724E-03	2.26836E-04
9.19092E-03	3.00852E-04
1.18447E-02	3.66387E-04
1.47028E-02	4.28777E-04

5.26053E-04	1.31623E-04
6.53947E-04	1.56906E-04
7.87237E-04	1.80762E-04
1.04513E-03	2.21906E-04
1.31395E-03	2.58669E-04
3.93513E-03	5.00076E-04
6.53171E-03	6.57063E-04
9.32158E-03	7.72058E-04
1.18393E-02	8.50103E-04
1.44251E-02	9.20447E-04
1.71470E-02	9.83573E-04
1.98007E-02	1.03581E-03
2.35433E-02	1.10250E-03
2.76261E-02	1.16524E-03
3.27975E-02	1.23435E-03
3.93980E-02	1.31152E-03
6.04242E-02	1.49651E-03
7.17879E-02	1.57118E-03
8.49888E-02	1.64277E-03
9.81897E-02	1.70421E-03
1.11663E-01	1.75865E-03
1.17923E-01	1.78073E-03
1.31124E-01	1.82498E-03
1.45278E-01	1.86691E-03
1.50994E-01	1.88187E-03
1.57798E-01	1.89893E-03
1.96857E-01	1.98938E-03
2.67897E-01	2.11251E-03
2.96476E-01	2.15017E-03
3.29410E-01	2.18840E-03
3.94803E-01	2.25451E-03
4.61011E-01	2.30999E-03
5.25927E-01	2.35555E-03
5.91660E-01	2.39536E-03
6.57937E-01	2.42969E-03
7.23329E-01	2.45992E-03
7.89674E-01	2.48654E-03
8.55066E-01	2.51023E-03
9.21275E-01	2.53138E-03
9.99732E-01	2.55472E-03
1.70843E-02	4.81529E-04
2.00783E-02	5.37883E-04
2.37529E-02	6.03003E-04
2.78357E-02	6.68248E-04
3.28030E-02	7.40997E-04
3.96075E-02	8.27465E-04
5.98853E-02	1.03309E-03
7.20655E-02	1.13202E-03
8.48582E-02	1.21716E-03
9.81272E-02	1.29499E-03
1.11941E-01	1.36587E-03
1.17997E-01	1.39437E-03
1.31606E-01	1.45290E-03
1.45147E-01	1.50438E-03
1.51067E-01	1.52587E-03
1.58280E-01	1.55001E-03
1.97747E-01	1.66328E-03
2.65316E-01	1.80801E-03
2.95665E-01	1.86037E-03
3.28463E-01	1.90899E-03
3.94740E-01	1.99307E-03
4.60677E-01	2.06046E-03
5.25797E-01	2.11727E-03
5.92142E-01	2.16661E-03
6.57874E-01	2.20984E-03
7.23947E-01	2.24803E-03
7.89543E-01	2.28277E-03
8.55616E-01	2.31390E-03
9.21212E-01	2.34182E-03
1.00008E+00	2.37303E-03
1.05172E+00	2.39175E-03
1.08554E+00	2.40365E-03

ZSM5 / N_2
-43°C

pressure (atm)	moles ads.
4.61974E-04	8.69992E-07
7.31447E-04	1.48568E-06
7.31447E-04	1.48568E-06
8.90658E-04	1.78906E-06
1.11053E-03	2.26198E-06
1.35145E-03	2.81074E-06
3.94737E-03	9.60114E-06
6.73039E-03	1.68198E-05
9.99671E-03	2.49487E-05
1.19700E-02	2.97983E-05
1.46238E-02	3.67360E-05
1.69374E-02	4.25002E-05
2.04758E-02	5.07585E-05
2.42863E-02	6.04444E-05
2.85051E-02	7.02820E-05
3.36087E-02	8.24708E-05
3.97328E-02	9.70108E-05
5.96022E-02	1.43379E-04
7.21908E-02	1.71031E-04
8.51875E-02	1.98568E-04
9.89329E-02	2.27046E-04
1.12270E-01	2.53690E-04
1.18734E-01	2.66316E-04
1.31799E-01	2.91282E-04
1.45068E-01	3.15843E-04
1.51464E-01	3.27313E-04
1.58201E-01	3.39025E-04
1.97191E-01	4.05430E-04
2.65373E-01	5.09235E-04
2.96811E-01	5.53168E-04
3.28997E-01	5.95101E-04
3.95069E-01	6.75248E-04
4.61142E-01	7.47626E-04
5.26398E-01	8.12247E-04
5.92199E-01	8.71951E-04
6.58067E-01	9.26912E-04
7.23868E-01	9.77746E-04
7.89804E-01	1.02461E-03
8.54993E-01	1.06745E-03
9.21201E-01	1.10829E-03
1.00054E+00	1.15393E-03

ZSM5 / N_2
0°C

pressure (atm)	moles ads.
7.41053E-04	1.11537E-07
1.03974E-03	1.33845E-07
1.24184E-03	1.15999E-07
1.36566E-03	5.79995E-08
3.99368E-03	1.28937E-06
6.53382E-03	2.51182E-06
9.25566E-03	3.48443E-06
1.23858E-02	4.72026E-06
1.49034E-02	5.97394E-06
1.72850E-02	7.33916E-06
1.99388E-02	8.47684E-06
2.39536E-02	1.05068E-05
2.79003E-02	1.22914E-05
3.31397E-02	1.49282E-05
3.98763E-02	1.81404E-05
6.01541E-02	2.88882E-05
7.29467E-02	3.52726E-05
8.59436E-02	4.15901E-05
9.87362E-02	4.77916E-05
1.12686E-01	5.47336E-05
1.18878E-01	5.79950E-05
1.31739E-01	6.42456E-05
1.44939E-01	7.04783E-05
1.51608E-01	7.38824E-05
1.58549E-01	7.70188E-05
1.98832E-01	9.62077E-05
2.63952E-01	1.26408E-04
2.96478E-01	1.41452E-04
3.29412E-01	1.56425E-04
3.95349E-01	1.85308E-04
4.59652E-01	2.12715E-04
5.25453E-01	2.40015E-04
5.91254E-01	2.66561E-04
6.57394E-01	2.92714E-04
7.22991E-01	3.17529E-04
7.88587E-01	3.41898E-04
8.54456E-01	3.65807E-04
9.20324E-01	3.89087E-04
9.99258E-01	4.16615E-04
1.05261E+00	4.35215E-04
1.08581E+00	4.46716E-04

ZSM5 / N_2 25°C		ZSM5 / C_2H_6 100°C	
pressure (atm)	moles ads.	pressure (atm)	moles ads.
7.48553E-04	5.35380E-08	5.00132E-04	7.85224E-07
1.05066E-03	6.24610E-08	8.24079E-04	1.31168E-06
1.20855E-03	3.12305E-08	1.17382E-03	1.83368E-06
1.36908E-03	8.92299E-09	1.37250E-03	2.08352E-06
3.98618E-03	6.11225E-07	3.93921E-03	7.40609E-06
6.59092E-03	1.23137E-06	6.94816E-03	1.38128E-05
9.44882E-03	2.00767E-06	9.19368E-03	1.85955E-05
1.22388E-02	2.75721E-06	1.27321E-02	2.59971E-05
1.47564E-02	3.41305E-06	1.45693E-02	2.97939E-05
1.74783E-02	4.01089E-06	1.70871E-02	3.49826E-05
2.00641E-02	4.30088E-06	2.05574E-02	4.22102E-05
2.38066E-02	5.39395E-06	2.34834E-02	4.81306E-05
2.85017E-02	6.44686E-06	2.83146E-02	5.78745E-05
3.30608E-02	7.70947E-06	3.36903E-02	6.90729E-05
3.95253E-02	9.27099E-06	4.06309E-02	8.27652E-05
6.04154E-02	1.44954E-05	5.92757E-02	1.18975E-04
7.27317E-02	1.76541E-05	7.17280E-02	1.42897E-04
8.48439E-02	2.06032E-05	8.50650E-02	1.66905E-04
9.86572E-02	2.40609E-05	9.85382E-02	1.91626E-04
1.12198E-01	2.72508E-05	1.12147E-01	2.16284E-04
1.18731E-01	2.88525E-05	1.18748E-01	2.27104E-04
1.31728E-01	3.21005E-05	1.30520E-01	2.46703E-04
1.45133E-01	3.54064E-05	1.45218E-01	2.69889E-04
1.51665E-01	3.68386E-05	1.50729E-01	2.80749E-04
1.58266E-01	3.83421E-05	1.58963E-01	2.91800E-04
1.97732E-01	4.83091E-05	1.97545E-01	3.51530E-04
2.64554E-01	6.46872E-05	2.67496E-01	4.45293E-04
2.96331E-01	7.24413E-05	2.95736E-01	4.82506E-04
3.29469E-01	8.03783E-05	3.30643E-01	5.20884E-04
3.95202E-01	9.62390E-05	3.95831E-01	5.91095E-04
4.59846E-01	1.11069E-04	4.61904E-01	6.55947E-04
5.25170E-01	1.26318E-04	5.27160E-01	7.11096E-04
5.90902E-01	1.41421E-04	5.91940E-01	7.63853E-04
6.58540E-01	1.57335E-04	6.59442E-01	8.11123E-04
7.22844E-01	1.71308E-04	7.24222E-01	8.53748E-04
7.88304E-01	1.85563E-04	7.89614E-01	8.93857E-04
8.54104E-01	1.99549E-04	8.55755E-01	9.30004E-04
9.19973E-01	2.13683E-04	9.21827E-01	9.64830E-04
1.00027E+00	2.31351E-04	1.00090E+00	1.00211E-03
1.05266E+00	2.42032E-04	1.05377E+00	1.02786E-03
1.08546E+00	2.49175E-04	1.08711E+00	1.03936E-03

ZSM5 / C_2H_6
75°C

pressure (atm)	moles ads.
4.10263E-04	1.82029E-06
6.83816E-04	3.18551E-06
8.38947E-04	3.94843E-06
1.05197E-03	4.99688E-06
1.34526E-03	6.44240E-06
3.91474E-03	1.92781E-05
6.60118E-03	3.24351E-05
9.18684E-03	4.15945E-05
1.19087E-02	5.54341E-05
1.44945E-02	6.78951E-05
1.77607E-02	8.30954E-05
1.98021E-02	9.23351E-05
2.41570E-02	1.12532E-04
2.74913E-02	1.26970E-04
3.35474E-02	1.53190E-04
3.98757E-02	1.79656E-04
5.95409E-02	2.57477E-04
7.23337E-02	3.02918E-04
8.53984E-02	3.46761E-04
9.85313E-02	3.90907E-04
1.12549E-01	4.33823E-04
1.18197E-01	4.50299E-04
1.30445E-01	4.85893E-04
1.45483E-01	5.25265E-04
1.50859E-01	5.40261E-04
1.58480E-01	5.59115E-04
1.97266E-01	6.47872E-04
2.65244E-01	7.77853E-04
2.96409E-01	8.29151E-04
3.28527E-01	8.77050E-04
3.95212E-01	9.64906E-04
4.59380E-01	1.03462E-03
5.25724E-01	1.09577E-03
5.91933E-01	1.14825E-03
6.57802E-01	1.19358E-03
7.23466E-01	1.23438E-03
7.89471E-01	1.27179E-03
8.55339E-01	1.30555E-03
9.21616E-01	1.33327E-03
1.00164E+00	1.36441E-03
1.05437E+00	1.38421E-03

ZSM5 / C_2H_6
55°C

pressure (atm)	moles ads.
1.90526E-04	1.79798E-06
3.57237E-04	3.13643E-06
4.99474E-04	4.47488E-06
6.09737E-04	5.49210E-06
7.11053E-04	6.42456E-06
8.04342E-04	7.29009E-06
1.08197E-03	1.00294E-05
1.34592E-03	1.25993E-05
3.91474E-03	3.80476E-05
6.68829E-03	6.45579E-05
9.20592E-03	8.79807E-05
1.18597E-02	1.12233E-04
1.45816E-02	1.35875E-04
1.71674E-02	1.57531E-04
1.98892E-02	1.80405E-04
2.36997E-02	2.12091E-04
2.79867E-02	2.44883E-04
3.28179E-02	2.82399E-04
4.00308E-02	3.33662E-04
5.94920E-02	4.57379E-04
7.18083E-02	5.27295E-04
8.54175E-02	5.96988E-04
9.86184E-02	6.58678E-04
1.11956E-01	7.15031E-04
1.18012E-01	7.38717E-04
1.31757E-01	7.88065E-04
1.44686E-01	8.31297E-04
1.51218E-01	8.51731E-04
1.57614E-01	8.72865E-04
1.97353E-01	9.78549E-04
2.63358E-01	1.11156E-03
2.95952E-01	1.16438E-03
3.28274E-01	1.20788E-03
3.93530E-01	1.28388E-03
4.61440E-01	1.34732E-03
5.27309E-01	1.39819E-03
5.91476E-01	1.43835E-03
6.58842E-01	1.47589E-03
7.24098E-01	1.50700E-03
7.88537E-01	1.53377E-03
8.56311E-01	1.56007E-03

1.08683E+00	1.39788E-03

9.20479E-01	1.58082E-03
1.00077E+00	1.60592E-03
1.05317E+00	1.61896E-03
1.08474E+00	1.62661E-03

ZSM5 / C_2H_6
40°C

pressure (atm)	moles ads.
1.71447E-04	3.02936E-06
3.42237E-04	5.62149E-06
4.71579E-04	7.91023E-06
5.84474E-04	9 89114E-06
6.64868E-04	1.12920E-05
8.09079E-04	1.38708E-05
1.06013E-03	1.82832E-05
1.30921E-03	2.26332E-05
3.95342E-03	6 84884E-05
6.55697E-03	1.11479E-04
9.48289E-03	1.57433E-04
1.18645E-02	1.91956E-04
1.49266E-02	2.35750E-04
1.71041E-02	2.67614E-04
2.00300E-02	3.05300E-04
2.35684E-02	3 50531E-04
2.79234E-02	4 01450E-04
3.30949E-02	4.58044E-04
3.96272E-02	5.23258E-04
5.99050E-02	6.94486E-04
7.22213E-02	7.81083E-04
8.52862E-02	8 58829E-04
9.84191E-02	9 27126E-04
1.11824E-01	9 89016E-04
1.18153E-01	1.01438E-03
1.32102E-01	1.06645E-03
1.45031E-01	1.10953E-03
1.51223E-01	1.12775E-03
1.57619E-01	1.14739E-03
1.98379E-01	1.24888E-03
2.65064E-01	1.36409E-03
2.96297E-01	1.40755E-03
3.28551E-01	1.44544E-03
3.95440E-01	1.50820E-03
4.59880E-01	1 55613E-03

ZSM5 / C_2H_6
25°C

pressure (atm)	moles ads.
1.35395E-04	3.18997E-06
3.51842E-04	9.27991E-06
4.24605E-04	1.18319E-05
5.55263E-04	1.62711E-05
6.55263E-04	1.96306E-05
8.15921E-04	2.51985E-05
1.06013E-03	3.33095E-05
1.31329E-03	4.16347E-05
3.97053E-03	1.27260E-04
6.64671E-03	2.06732E-04
9.77684E-03	2.32484E-04
1.18183E-02	2.89765E-04
1.44039E-02	3.55555E-04
1.69897E-02	4.15548E-04
1.98476E-02	4.78246E-04
2.37943E-02	5.55305E-04
2.78091E-02	6.25390E-04
3.27764E-02	7.01468E-04
3.92408E-02	7.91394E-04
5.94505E-02	9.96154E-04
7.16988E-02	1.08989E-03
8.48317E-02	1.16700E-03
9.84409E-02	1.23480E-03
1.10757E-01	1.28705E-03
1.18038E-01	1.31439E-03
1.30423E-01	1.35598E-03
1.45120E-01	1.39806E-03
1.50904E-01	1.41257E-03
1.57981E-01	1.42923E-03
1.97856E-01	1.50864E-03
2.65970E-01	1.60158E-03
2.96115E-01	1.63399E-03
3.28777E-01	1.66252E-03
3.94373E-01	1.70999E-03
4.60378E-01	1.74652E-03

5.25748E-01	1.59670E-03
5.92161E-01	1.62990E-03
6.57485E-01	1.65806E-03
7.23830E-01	1.68193E-03
7.90652E-01	1.70369E-03
8.56860E-01	1.72287E-03
9.23137E-01	1.73919E-03
1.00241E+00	1.75735E-03
1.05467E+00	1.76949E-03
1.08774E+00	1.77501E-03

5.25498E-01	1.77693E-03
5.92047E-01	1.80379E-03
6.58120E-01	1.82593E-03
7.23376E-01	1.84609E-03
7.89653E-01	1.86465E-03
8.56950E-01	1.88117E-03
9.22887E-01	1.89614E-03
1.00216E+00	1.91250E-03
1.05476E+00	1.92253E-03
1.08729E+00	1.92902E-03

ZSM5 / C_3H_8
175°C

pressure (atm)	moles ads.
5.16447E-04	7.09378E-07
8.55395E-04	1.20014E-06
1.09421E-03	1.53922E-06
1.36711E-03	1.93183E-06
3.97934E-03	5.93825E-06
6.66579E-03	9.90899E-06
9.99934E-03	1.47051E-05
1.20408E-02	1.73508E-05
1.44224E-02	2.08620E-05
1.70082E-02	2.43910E-05
1.95938E-02	2.80450E-05
2.45612E-02	3.48220E-05
2.77593E-02	3.88864E-05
3.39516E-02	4.71313E-05
3.93953E-02	5.38458E-05
5.88564E-02	7.82547E-05
7.19213E-02	9.32498E-05
8.54625E-02	1.08704E-04
9.81871E-02	1.22330E-04
1.11252E-01	1.36147E-04
1.18669E-01	1.43910E-04
1.31394E-01	1.56215E-04
1.43982E-01	1.68850E-04
1.51807E-01	1.75622E-04
1.57659E-01	1.81726E-04
1.97806E-01	2.16427E-04
2.63403E-01	2.68712E-04
2.96133E-01	2.90912E-04

ZSM5 / C_3H_8
150°C

pressure (atm)	moles ads.
4.69474E-04	1.49460E-06
7.92763E-04	2.48952E-06
1.14118E-03	3.63166E-06
1.30789E-03	4.13135E-06
3.97868E-03	1.34737E-05
6.75487E-03	2.30570E-05
1.00212E-02	3.36575E-05
1.19945E-02	4.00776E-05
1.53287E-02	5.07540E-05
1.72341E-02	5.64692E-05
1.97517E-02	6.41340E-05
2.45150E-02	7.81164E-05
2.76451E-02	8.69055E-05
3.38372E-02	1.04180E-04
4.09821E-02	1.22562E-04
5.90143E-02	1.67770E-04
7.20791E-02	1.98376E-04
8.56883E-02	2.26479E-04
9.81408E-02	2.50973E-04
1.11138E-01	2.75466E-04
1.18691E-01	2.88280E-04
1.30803E-01	3.11140E-04
1.45024E-01	3.30642E-04
1.51081E-01	3.44240E-04
1.58906E-01	3.53467E-04
1.99053E-01	4.07237E-04
2.66487E-01	4.85304E-04
2.97244E-01	5.19715E-04

3.28047E-01	3.13086E-04
3.96501E-01	3.54743E-04
4.59716E-01	3.89141E-04
5.25856E-01	4.23048E-04
5.91521E-01	4.54845E-04
6.57934E-01	4.83448E-04
7.23666E-01	5.08771E-04
7.89399E-01	5.31904E-04
8.54519E-01	5.55787E-04
9.21612E-01	5.77768E-04
1.00170E+00	6.01446E-04

3.30314E-01	5.48728E-04
3.96591E-01	6.05354E-04
4.61030E-01	6.52191E-04
5.25198E-01	6.99045E-04
5.94128E-01	7.35241E-04
6.59929E-01	7.70929E-04
7.26274E-01	8.02708E-04
7.91666E-01	8.36303E-04
8.60189E-01	8.56112E-04
9.24968E-01	8.79682E-04
1.00513E+00	9.05260E-04

ZSM5 / C_3H_8
125°C

pressure (atm)	moles ads.
3.34737E-04	1.26260E-06
5.79737E-04	2.20844E-06
7.64868E-04	2.88659E-06
9.27500E-04	3.41305E-06
1.06697E-03	3.89043E-06
1.31803E-03	5.21103E-06
3.97934E-03	2.10806E-05
6.84342E-03	3.75970E-05
9.83737E-03	5.27304E-05
1.24232E-02	6.56911E-05
1.52130E-02	7.87722E-05
1.77308E-02	9.20853E-05
1.96361E-02	1.01691E-04
2.38549E-02	1.21014E-04
2.84820E-02	1.40198E-04
3.29730E-02	1.59427E-04
3.97776E-02	1.87601E-04
6.06678E-02	2.63398E-04
7.25759E-02	3.02030E-04
8.56407E-02	3.39667E-04
9.82972E-02	3.75007E-04
1.12791E-01	4.09887E-04
1.19256E-01	4.25123E-04
1.30483E-01	4.51245E-04
1.45929E-01	4.81155E-04
1.51305E-01	4.94740E-04
1.59471E-01	5.08272E-04
1.97781E-01	5.73053E-04

ZSM5 / C_3H_8
75°C

pressure (atm)	moles ads.
1.08816E-04	3.37735E-06
2.07500E-04	6.74578E-06
3.15789E-04	9.85099E-06
4.47105E-04	1.50397E-05
5.51842E-04	1.91354E-05
6.81842E-04	2.45382E-05
7.96184E-04	2.93879E-05
1.05263E-03	3.94709E-05
1.30855E-03	4.90051E-05
3.99632E-03	1.38712E-04
6.67868E-03	2.13987E-04
9.12842E-03	2.68600E-04
1.19183E-02	3.26024E-04
1.45721E-02	3.76309E-04
1.72939E-02	4.25216E-04
1.97436E-02	4.64379E-04
2.36222E-02	5.20242E-04
2.77730E-02	5.75350E-04
3.33528E-02	6.36839E-04
3.93408E-02	6.92955E-04
5.96186E-02	8.45869E-04
7.23432E-02	9.17351E-04
8.55441E-02	9.78099E-04
9.80646E-02	1.02643E-03
1.11334E-01	1.06783E-03
1.19431E-01	1.09218E-03
1.31203E-01	1.12224E-03
1.45833E-01	1.15487E-03

2.67119E-01	6.70228E-04
2.95495E-01	7.06996E-04
3.30470E-01	7.43879E-04
3.94161E-01	8.06295E-04
4.63773E-01	8.57027E-04
5.25014E-01	9.06085E-04
5.92720E-01	9.43732E-04
6.59269E-01	9.78607E-04
7.25818E-01	1.00929E-03
7.91755E-01	1.03714E-03
8.55582E-01	1.05965E-03
9.22471E-01	1.08306E-03
1.00038E+00	1.10549E-03
1.50936E-01	1.16653E-03
1.58558E-01	1.18087E-03
1.97072E-01	1.24163E-03
2.64914E-01	1.31835E-03
2.97235E-01	1.34941E-03
3.29898E-01	1.37128E-03
3.94133E-01	1.40962E-03
4.61158E-01	1.44182E-03
5.28252E-01	1.46662E-03
5.94733E-01	1.48793E-03
6.60873E-01	1.50720E-03
7.27627E-01	1.52112E-03
7.93019E-01	1.53678E-03
8.59908E-01	1.54689E-03
9.25164E-01	1.55911E-03
1.00580E+00	1.56810E-03

ZSM5 / DME
200oC

pressure (atm)	moles ads.
4.42105E-05	4.33211E-06
7.01316E-05	8.18239E-06
1.29342E-04	2.61444E-05
1.52368E-04	2.97939E-05
2.72895E-04	4.96208E-05
4.06184E-04	6.32150E-05
5.37500E-04	8.35371E-05
6.79079E-04	1.04114E-04
8.00921E-04	1.99835E-04
1.14039E-03	2.58441E-04
1.36711E-03	3.49554E-04
4.71289E-03	4.73003E-04
6.62842E-03	4.97930E-04
9.41895E-03	5.23481E-04
1.24130E-02	5.43129E-04
1.46584E-02	5.55751E-04
1.71762E-02	5.67212E-04
2.05104E-02	5.81967E-04
2.40488E-02	5.90823E-04
2.79275E-02	6.02204E-04
3.39155E-02	6.18627E-04
4.00396E-02	6.28219E-04
5.94328E-02	6.57361E-04

ZSM5 / DME
175oC

pressure (atm)	moles ads.
4.63158E-05	4.59534E-06
7.48684E-05	8.56607E-06
1.08816E-04	2.39136E-05
1.43553E-04	4.57973E-05
2.71447E-04	1.10797E-04
4.08947E-04	1.85906E-04
5.36842E-04	2.34505E-04
6.66842E-04	4.17694E-04
8.65526E-04	4.48550E-04
1.07447E-03	4.77960E-04
1.32895E-03	4.96203E-04
3.99974E-03	5.61292E-04
6.62500E-03	5.84844E-04
9.89053E-03	6.01686E-04
1.18638E-02	6.09869E-04
1.45176E-02	6.32324E-04
1.79199E-02	6.45373E-04
2.09820E-02	6.56897E-04
2.36358E-02	6.66815E-04
2.77866E-02	6.75961E-04
3.30942E-02	6.89631E-04
3.94905E-02	7.02463E-04
5.97003E-02	7.34309E-04

7.30420E-02	6.72870E-04
8.46779E-02	6.87285E-04
9.92397E-02	6.99474E-04
1.12305E-01	7.12220E-04
1.18565E-01	7.19434E-04
1.32514E-01	7.27510E-04
1.45307E-01	7.41206E-04
1.52792E-01	7.43308E-04
1.58644E-01	7.51731E-04
1.98927E-01	7.72829E-04
2.65068E-01	8.11404E-04
2.98887E-01	8.24761E-04
3.30120E-01	8.45846E-04
3.98710E-01	8.67917E-04
4.63150E-01	9.01486E-04
5.32081E-01	9.19921E-04
5.96248E-01	9.44994E-04
6.61096E-01	9.74900E-04
7.30095E-01	9.89382E-04
7.94534E-01	1.00884E-03
8.60403E-01	1.02852E-03
9.26339E-01	1.04742E-03
1.00412E+00	1.07993E-03

7.26970E-02	7.55822E-04
8.64424E-02	7.72330E-04
9.94391E-02	7.90988E-04
1.12164E-01	8.05559E-04
1.18968E-01	8.15379E-04
1.31965E-01	8.27875E-04
1.45030E-01	8.44669E-04
1.52515E-01	8.49616E-04
1.58299E-01	8.59963E-04
1.97561E-01	8.90742E-04
2.63702E-01	9.39913E-04
2.95003E-01	9.68448E-04
3.30728E-01	9.87985E-04
3.96800E-01	1.02805E-03
4.62669E-01	1.06720E-03
5.29422E-01	1.10129E-03
5.95427E-01	1.13379E-03
6.61363E-01	1.16515E-03
7.27708E-01	1.19330E-03
7.93373E-01	1.22188E-03
8.60262E-01	1.24449E-03
9.25246E-01	1.27089E-03
1.00588E+00	1.29721E-03

ZSM5 / DME
150°C

pressure (atm)	moles ads.
5.44737E-05	4.12242E-06
8.50000E-05	7.87900E-06
1.16316E-04	1.18230E-05
1.42895E-04	2.22763E-05
2.72237E-04	2.98349E-04
4.71579E-04	3.60427E-04
5.28684E-04	4.92518E-04
7.49868E-04	5.22209E-04
8.02237E-04	5.44129E-04
1.11118E-03	5.64295E-04
1.34395E-03	5.78513E-04
4.34605E-03	6.28210E-04
6.61132E-03	6.47189E-04
9.74145E-03	6.63590E-04
1.25993E-02	6.76983E-04
1.46408E-02	6.83675E-04
1.75667E-02	6.94410E-04
1.97442E-02	7.02498E-04

FSG / CH_4
-17°C

pressure (atm)	moles ads.
3.92895E-03	2.67690E-07
6.73447E-03	9.41376E-07
9.25289E-03	1.36076E-06
1.19747E-02	2.10137E-06
1.46286E-02	2.56982E-06
1.72143E-02	3.50228E-06
1.99362E-02	4.24288E-06
2.37467E-02	5.13072E-06
2.77614E-02	6.33979E-06
3.30691E-02	7.77193E-06
3.95334E-02	9.37361E-06
5.99472E-02	1.52762E-05
7.26038E-02	1.88587E-05
8.56686E-02	2.23655E-05
9.85974E-02	2.58276E-05
1.11662E-01	2.92674E-05
1.18671E-01	3.10386E-05

2.47116E-02	7.15945E-04
2.79778E-02	7.25141E-04
3.39659E-02	7.41929E-04
3.94776E-02	7.54247E-04
5.88026E-02	7.95507E-04
7.28201E-02	8.19831E-04
8.62933E-02	8.44441E-04
9.79972E-02	8.66833E-04
1.12015E-01	8.85911E-04
1.18071E-01	8.99416E-04
1.31680E-01	9.16610E-04
1.43520E-01	9.37673E-04
1.52638E-01	9.46944E-04
1.57742E-01	9.59267E-04
1.98093E-01	1.00403E-03
2.63281E-01	1.07432E-03
2.96964E-01	1.10417E-03
3.30715E-01	1.13485E-03
3.95631E-01	1.18913E-03
4.61227E-01	1.23066E-03
5.28320E-01	1.27352E-03
5.92420E-01	1.30934E-03
6.58152E-01	1.34073E-03
7.24974E-01	1.37180E-03
7.91386E-01	1.39950E-03
8.57391E-01	1.42510E-03
9.23872E-01	1.44762E-03
1.00172E+00	1.48128E-03

1.31464E-01	3.41661E-05
1.44528E-01	3.76773E-05
1.51605E-01	3.94619E-05
1.58138E-01	4.08495E-05
1.97264E-01	5.03257E-05
2.63745E-01	6.60257E-05
2.96203E-01	7.38824E-05
3.29273E-01	8.12216E-05
3.94870E-01	9.64397E-05
4.61011E-01	1.10471E-04
5.26743E-01	1.23878E-04
5.92271E-01	1.37494E-04
6.58140E-01	1.51276E-04
7.24009E-01	1.64295E-04
7.89673E-01	1.77220E-04
8.55610E-01	1.89975E-04
9.21274E-01	2.02374E-04
1.00014E+00	2.16824E-04

FSG / CH_4
-44°C

pressure (atm)	moles ads.
6.87895E-04	2.40921E-07
1.04184E-03	4.77380E-07
1.17789E-03	5.48764E-07
1.31539E-03	6.20148E-07
3.93921E-03	2.59213E-06
6.65632E-03	4.64442E-06
9.31000E-03	6.86178E-06
1.19638E-02	8.82038E-06
1.45496E-02	1.07433E-05
1.72714E-02	1.27331E-05
1.98572E-02	1.46605E-05
2.37358E-02	1.71589E-05

FSG / CH_4
-62°C

pressure (atm)	moles ads.
5.93421E-04	6.64763E-07
9.15263E-04	1.17784E-06
1.08737E-03	1.43214E-06
1.42697E-03	1.94521E-06
3.95618E-03	5.99625E-06
6.62158E-03	1.01722E-05
9.20737E-03	1.38529E-05
1.18611E-02	1.75471E-05
1.52634E-02	2.27046E-05
1.73047E-02	2.57518E-05
1.98225E-02	2.91603E-05
2.46538E-02	3.61872E-05

2.76145E-02	1.99206E-05
3.28539E-02	2.35389E-05
3.93864E-02	2.79870E-05
5.93920E-02	4.17730E-05
7.25929E-02	5.02097E-05
8.56578E-02	5.83207E-05
9.83824E-02	6.60257E-05
1.11583E-01	7.39404E-05
1.18592E-01	7.78487E-05
1.31317E-01	8.55447E-05
1.44586E-01	9.29642E-05
1.51458E-01	9.67297E-05
1.58059E-01	1.00379E-04
1.97662E-01	1.21576E-04
2.63394E-01	1.55198E-04
2.96260E-01	1.71183E-04
3.29195E-01	1.87129E-04
3.95199E-01	2.16922E-04
4.60591E-01	2.45650E-04
5.26528E-01	2.73200E-04
5.92193E-01	2.99933E-04
6.58061E-01	3.25895E-04
7.23794E-01	3.51062E-04
7.89730E-01	3.74980E-04
8.55191E-01	3.98697E-04
9.21331E-01	4.21375E-04
9.99856E-01	4.48345E-04

2.77839E-02	4.05104E-05
3.26832E-02	4.65111E-05
4.07807E-02	5.68573E-05
5.96975E-02	7.96957E-05
7.22861E-02	9.41376E-05
8.54189E-02	1.08468E-04
9.80754E-02	1.21362E-04
1.11140E-01	1.34603E-04
1.18693E-01	1.41960E-04
1.31078E-01	1.53712E-04
1.44007E-01	1.65673E-04
1.51560E-01	1.72513E-04
1.58160E-01	1.77795E-04
1.96810E-01	2.10676E-04
2.64448E-01	2.63108E-04
2.95885E-01	2.85772E-04
3.29160E-01	3.08932E-04
3.95028E-01	3.52414E-04
4.60761E-01	3.93393E-04
5.26561E-01	4.32350E-04
5.92362E-01	4.69171E-04
6.58026E-01	5.03846E-04
7.23691E-01	5.37981E-04
7.89628E-01	5.71397E-04
8.55564E-01	6.02958E-04
9.20956E-01	6.34376E-04
1.00043E+00	6.70358E-04

FSG / CH_4
-93°C

pressure (atm)	moles ads.
2.76316E-04	2.66798E-06
4.95395E-04	4.73365E-06
6.61447E-04	6.42456E-06
8.85921E-04	8.65530E-06
1.06895E-03	1.04265E-05
1.31263E-03	1.27733E-05
3.99697E-03	3.57366E-05
6.52079E-03	5.42830E-05
9.78711E-03	7.49487E-05
1.25770E-02	9.16748E-05
1.46183E-02	1.03128E-04
1.78164E-02	1.20112E-04

FSG / CO
-17°C

pressure (atm)	moles ads.
1.08947E-03	1.33845E-08
1.33776E-03	8.92299E-09
3.98539E-03	5.30918E-07
6.59026E-03	1.05737E-06
9.38079E-03	1.39199E-06
1.18986E-02	2.06567E-06
1.46884E-02	2.40029E-06
1.73422E-02	3.16766E-06
1.99280E-02	3.36397E-06
2.39426E-02	4.01535E-06
2.77533E-02	4.79165E-06
3.30608E-02	5.54118E-06

1.97899E-02	1.29879E-04
2.42128E-02	1.50866E-04
2.74791E-02	1.65093E-04
3.31268E-02	1.88351E-04
3.95912E-02	2.13389E-04
5.87122E-02	2.77523E-04
7.17770E-02	3.15910E-04
8.55224E-02	3.53422E-04
9.87913E-02	3.86995E-04
1.11992E-01	4.18314E-04
1.18525E-01	4.32895E-04
1.31658E-01	4.61631E-04
1.43429E-01	4.86183E-04
1.51595E-01	5.02097E-04
1.57923E-01	5.14638E-04
1.97118E-01	5.86745E-04
2.63939E-01	6.94646E-04
2.95104E-01	7.40533E-04
3.28923E-01	7.87731E-04
3.95200E-01	8.73258E-04
4.60660E-01	9.51196E-04
5.26393E-01	1.02403E-03
5.92125E-01	1.09294E-03
6.58062E-01	1.15795E-03
7.23726E-01	1.22012E-03
7.89731E-01	1.27936E-03
8.55259E-01	1.33613E-03
9.21196E-01	1.39071E-03
1.00013E+00	1.45343E-03

3.95253E-02	6.81271E-06
5.90545E-02	1.01990E-05
7.25275E-02	1.28536E-05
8.57286E-02	1.50843E-05
9.87933E-02	1.74578E-05
1.11994E-01	1.96618E-05
1.18663E-01	2.08084E-05
1.31932E-01	2.30570E-05
1.44861E-01	2.51182E-05
1.51529E-01	2.62604E-05
1.58198E-01	2.71928E-05
1.96576E-01	3.37245E-05
2.62376E-01	4.43785E-05
2.96331E-01	4.99777E-05
3.29265E-01	5.54073E-05
3.93841E-01	6.57714E-05
4.60118E-01	7.61131E-05
5.25918E-01	8.62898E-05
5.91651E-01	9.62479E-05
6.57451E-01	1.05987E-04
7.23252E-01	1.15945E-04
7.89121E-01	1.25199E-04
8.54989E-01	1.34447E-04
9.20722E-01	1.43883E-04
9.99315E-01	1.54194E-04

FSG / CO
-44°C

pressure (atm)	moles ads.
6.15132E-04	1.73998E-07
9.28816E-04	3.12305E-07
1.14184E-03	3.92612E-07
1.31329E-03	4.50611E-07
3.95829E-03	1.80244E-06
6.63579E-03	3.14982E-06
9.22158E-03	4.08227E-06
1.18754E-02	5.26457E-06
1.52778E-02	7.08040E-06
1.72511E-02	7.91023E-06

FSG / CO
-62°C

pressure (atm)	moles ads.
5.39605E-04	6.69225E-07
8.49868E-04	1.08861E-06
1.05408E-03	1.34291E-06
1.38263E-03	1.73552E-06
3.97658E-03	4.66673E-06
6.58000E-03	7.45962E-06
1.00497E-02	1.05827E-05
1.18189E-02	1.24119E-05
1.44728E-02	1.54100E-05
1.71264E-02	1.78817E-05

1.98368E-02	9.08807E-06
2.35793E-02	1.09530E-05
2.75261E-02	1.28536E-05
3.27655E-02	1.52048E-05
3.95701E-02	1.83144E-05
5.91674E-02	2.72821E-05
7.23683E-02	3.29303E-05
8.55012E-02	3.83153E-05
9.82258E-02	4.41822E-05
1.11427E-01	4.95672E-05
1.18572E-01	5.22397E-05
1.31160E-01	5.75578E-05
1.44361E-01	6.27688E-05
1.51506E-01	6.56866E-05
1.58243E-01	6.78415E-05
1.96757E-01	8.25912E-05
2.64122E-01	1.07384E-04
2.96172E-01	1.18970E-04
3.29310E-01	1.30401E-04
3.94907E-01	1.52494E-04
4.61115E-01	1.73963E-04
5.25691E-01	1.93522E-04
5.92172E-01	2.13474E-04
6.58245E-01	2.32025E-04
7.23637E-01	2.50232E-04
7.89778E-01	2.67556E-04
8.55374E-01	2.84023E-04
9.21243E-01	2.99777E-04
1.00004E+00	3.18288E-04

1.97122E-02	2.03534E-05
2.35909E-02	2.40564E-05
2.76057E-02	2.75051E-05
3.25730E-02	3.24083E-05
4.08746E-02	3.96449E-05
5.90429E-02	5.59159E-05
7.21758E-02	6.67440E-05
8.53767E-02	7.73267E-05
9.80333E-02	8.77933E-05
1.11234E-01	9.78228E-05
1.18515E-01	1.03609E-04
1.31172E-01	1.12813E-04
1.44373E-01	1.22575E-04
1.51518E-01	1.27822E-04
1.58118E-01	1.32466E-04
1.97449E-01	1.59195E-04
2.63657E-01	2.00745E-04
2.95979E-01	2.19858E-04
3.29118E-01	2.38940E-04
3.95054E-01	2.74971E-04
4.60719E-01	3.09101E-04
5.26519E-01	3.41255E-04
5.92252E-01	3.72196E-04
6.58052E-01	4.02490E-04
7.24057E-01	4.31217E-04
7.89517E-01	4.58499E-04
8.55386E-01	4.84528E-04
9.21118E-01	5.10293E-04
1.00026E+00	5.40109E-04

FSG / CO
-93°C

pressure (atm)	moles ads.
3.59342E-04	1.66860E-06
6.03553E-04	3.22120E-06
7.90000E-04	4.34996E-06
1.05066E-03	5.91148E-06
1.35553E-03	7.69608E-06
3.97526E-03	2.23833E-05
6.61684E-03	3.57455E-05
9.88303E-03	5.05488E-05
1.17883E-02	5.87758E-05
1.52587E-02	7.27090E-05

FSG / N_2
-17°C

pressure (atm)	moles ads.
6.53855E-03	1.96306E-07
9.87276E-03	4.72919E-07
1.23225E-02	6.60302E-07
1.45680E-02	1.26707E-06
1.78342E-02	1.52137E-06
2.00117E-02	1.60614E-06
2.38903E-02	1.84706E-06
2.79730E-02	1.91398E-06
3.29404E-02	2.81074E-06
3.98811E-02	3.21674E-06

1.70959E-02	8.04809E-05
1.96816E-02	9.02606E-05
2.39005E-02	1.05211E-04
2.83916E-02	1.20237E-04
3.36311E-02	1.37285E-04
4.03676E-02	1.57353E-04
5.91483E-02	2.07513E-04
7.18049E-02	2.37999E-04
8.50058E-02	2.67360E-04
9.88192E-02	2.95811E-04
1.12020E-01	3.20982E-04
1.18416E-01	3.32814E-04
1.31685E-01	4.07027E-04
1.48016E-01	4.32408E-04
1.51691E-01	4.37526E-04
1.57815E-01	4.47542E-04
1.97622E-01	5.13184E-04
2.64920E-01	6.09641E-04
2.95132E-01	6.48389E-04
3.28815E-01	6.89551E-04
3.95228E-01	7.63920E-04
4.60756E-01	8.30280E-04
5.26216E-01	8.91800E-04
5.92153E-01	9.49772E-04
6.58022E-01	1.00366E-03
7.23754E-01	1.05398E-03
7.89555E-01	1.10172E-03
8.55423E-01	1.14695E-03
9.21224E-01	1.18922E-03
9.99885E-01	1.23837E-03

5.87979E-02	5.20211E-06
7.26793E-02	6.50932E-06
8.57442E-02	8.02177E-06
9.87409E-02	9.51637E-06
1.11874E-01	1.10288E-05
1.18814E-01	1.14616E-05
1.31743E-01	1.28937E-05
1.45012E-01	1.42456E-05
1.51681E-01	1.48300E-05
1.58281E-01	1.56375E-05
1.97748E-01	1.97154E-05
2.63617E-01	2.55956E-05
2.96211E-01	2.85714E-05
3.29349E-01	3.20023E-05
3.95286E-01	3.83912E-05
4.59657E-01	4.41911E-05
5.25254E-01	5.04551E-05
5.91258E-01	5.63755E-05
6.56923E-01	6.22334E-05
7.22723E-01	6.81226E-05
7.88320E-01	7.41590E-05
8.54324E-01	8.01062E-05
9.19989E-01	8.59284E-05
1.00028E+00	9.32721E-05

FSG / N_2
-44°C

pressure (atm)	moles ads.
6.82500E-04	5.79995E-08
9.17895E-04	1.15999E-07
1.06421E-03	1.42768E-07
1.30579E-03	1.96306E-07
3.98474E-03	8.52146E-07
6.59092E-03	1.47676E-06
9.24474E-03	2.04783E-06
1.20346E-02	2.87767E-06
1.47564E-02	3.69412E-06

FSG / N_2
-62°C

pressure (atm)	moles ads.
6.89342E-04	9.36914E-08
9.67632E-04	1.82921E-07
1.14855E-03	2.27536E-07
1.38882E-03	2.89997E-07
3.93447E-03	1.39645E-06
6.63987E-03	2.58767E-06
9.22566E-03	3.82796E-06
1.19475E-02	4.82288E-06
1.45333E-02	6.31748E-06

1.74783E-02	4.51950E-06
2.01321E-02	5.08165E-06
2.43509E-02	6.08548E-06
2.77533E-02	6.98224E-06
3.27887E-02	8.33854E-06
3.99336E-02	9.69930E-06
5.97349E-02	1.43348E-05
7.24595E-02	1.73731E-05
8.55924E-02	2.04560E-05
9.86572E-02	2.35344E-05
1.11722E-01	2.66084E-05
1.18799E-01	2.82145E-05
1.31455E-01	3.07486E-05
1.45269E-01	3.37111E-05
1.51597E-01	3.52191E-05
1.58538E-01	3.65575E-05
1.97800E-01	4.51013E-05
2.64009E-01	5.83252E-05
2.96263E-01	6.52806E-05
3.29538E-01	7.20175E-05
3.95270E-01	8.53931E-05
4.61071E-01	9.82600E-05
5.26667E-01	1.10743E-04
5.92468E-01	1.22887E-04
6.58268E-01	1.34572E-04
7.24069E-01	1.46297E-04
7.90209E-01	1.58057E-04
8.55806E-01	1.69002E-04
9.21266E-01	1.80182E-04
1.00040E+00	1.93183E-04

1.75272E-02	7.10270E-06
1.99089E-02	8.56607E-06
2.39237E-02	9.79299E-06
2.78022E-02	1.15151E-05
3.29738E-02	1.34425E-05
3.93020E-02	1.61194E-05
5.96478E-02	2.43776E-05
7.26446E-02	2.95262E-05
8.57775E-02	3.46703E-05
9.85021E-02	4.00330E-05
1.11567E-01	4.51950E-05
1.18848E-01	4.80369E-05
1.31573E-01	5.31454E-05
1.45182E-01	5.81065E-05
1.51646E-01	6.05514E-05
1.58451E-01	6.30053E-05
1.97577E-01	7.74828E-05
2.63718E-01	1.00928E-04
2.96516E-01	1.11346E-04
3.29110E-01	1.22084E-04
3.95455E-01	1.43134E-04
4.60983E-01	1.63135E-04
5.26648E-01	1.82904E-04
5.92516E-01	2.01927E-04
6.58657E-01	2.20742E-04
7.24049E-01	2.38382E-04
7.89714E-01	2.55813E-04
8.55651E-01	2.72249E-04
9.21383E-01	2.88650E-04
1.00066E+00	3.07901E-04

FSG / N_2
-94°C

pressure (atm)	moles ads.
5.66842E-04	7.62916E-07
8.53947E-04	1.35630E-06
1.12895E-03	1.88721E-06
1.32355E-03	2.23967E-06
3.97803E-03	7.20532E-06
6.61197E-03	1.19657E-05
1.01504E-02	1.77077E-05
1.20557E-02	2.07950E-05
1.46414E-02	2.52521E-05

FSG / C_2H_6
100°C

pressure (atm)	moles ads.
1.13974E-03	4.46150E-09
4.10789E-03	2.63228E-07
6.73526E-03	5.17534E-07
9.66118E-03	7.58455E-07
1.23150E-02	7.58455E-07
1.49688E-02	1.17784E-06
1.75545E-02	1.32953E-06
2.02763E-02	1.39199E-06
2.42911E-02	1.73552E-06

1.74993E-02	2.98831E-05
1.97449E-02	3.36620E-05
2.47804E-02	4.13135E-05
2.77743E-02	4.59133E-05
3.26737E-02	5.35960E-05
4.08392E-02	6.52762E-05
5.93478E-02	9.08450E-05
7.20043E-02	1.07446E-04
8.53413E-02	1.23592E-04
9.78618E-02	1.38699E-04
1.11131E-01	1.54078E-04
1.18820E-01	1.62238E-04
1.30864E-01	1.75368E-04
1.43861E-01	1.89261E-04
1.51618E-01	1.96930E-04
1.58151E-01	2.03864E-04
1.97345E-01	2.41581E-04
2.63486E-01	2.99273E-04
2.96012E-01	3.25422E-04
3.29082E-01	3.51169E-04
3.95223E-01	3.99407E-04
4.60956E-01	4.44530E-04
5.26756E-01	4.86464E-04
5.92353E-01	5.26720E-04
6.58153E-01	5.65165E-04
7.23954E-01	6.01276E-04
7.89618E-01	6.37428E-04
8.55895E-01	6.71063E-04
9.21015E-01	7.03748E-04
1.00097E+00	7.41278E-04

FSG / C_2H_6
75°C

pressure (atm)	moles ads.
1.21782E-02	5.93379E-07
1.48320E-02	1.03953E-06
1.75538E-02	1.32060E-06
2.02076E-02	1.76675E-06
2.43584E-02	2.25306E-06
2.81691E-02	2.64567E-06
3.36128E-02	3.66735E-06
4.02812E-02	4.70242E-06
6.06270E-02	7.89239E-06
7.38279E-02	9.83314E-06
2.83058E-02	2.08352E-06
3.37495E-02	2.61890E-06
4.02818E-02	3.47104E-06
6.08318E-02	5.38503E-06
7.38286E-02	6.83501E-06
8.64851E-02	7.99054E-06
1.00367E-01	9.34684E-06
1.13636E-01	1.08281E-05
1.20168E-01	1.14660E-05
1.33641E-01	1.26707E-05
1.47250E-01	1.36165E-05
1.53034E-01	1.44374E-05
1.59703E-01	1.52316E-05
2.00258E-01	1.93763E-05
2.67148E-01	2.54573E-05
2.98789E-01	2.85759E-05
3.31927E-01	3.18149E-05
3.99021E-01	3.73561E-05
4.64345E-01	4.38788E-05
5.30418E-01	4.87329E-05
5.95810E-01	5.50950E-05
6.61951E-01	5.98019E-05
7.27275E-01	6.67217E-05
7.93688E-01	7.10226E-05
8.59012E-01	7.70991E-05
9.25017E-01	8.18729E-05
1.00449E+00	8.74186E-05
1.05567E+00	9.31739E-05
1.08826E+00	9.49987E-05

FSG / C_2H_6
55°C

pressure (atm)	moles ads.
1.37184E-03	8.92299E-09
3.96579E-03	6.73686E-07
6.56368E-03	1.35183E-06
9.28553E-03	1.87383E-06
1.22116E-02	2.54305E-06
1.47972E-02	2.97136E-06
1.75191E-02	3.70304E-06
1.99688E-02	4.44365E-06
2.39155E-02	5.43857E-06
2.78621E-02	6.44240E-06

8.69608E-02	1.19568E-05
1.00298E-01	1.42813E-05
1.13635E-01	1.65745E-05
1.20099E-01	1.74445E-05
1.33504E-01	2.00366E-05
1.46841E-01	2.16338E-05
1.53102E-01	2.25038E-05
1.59770E-01	2.38110E-05
2.00053E-01	2.93165E-05
2.66534E-01	3.87927E-05
2.98380E-01	4.34327E-05
3.31450E-01	4.80816E-05
3.98067E-01	5.77095E-05
4.64004E-01	6.60882E-05
5.29668E-01	7.52788E-05
5.95673E-01	8.30151E-05
6.61269E-01	9.15187E-05
7.27138E-01	9.93799E-05
7.92871E-01	1.07326E-04
8.58739E-01	1.14919E-04
9.24336E-01	1.23396E-04
1.00415E+00	1.31320E-04
1.05546E+00	1.38463E-04
1.08792E+00	1.42554E-04

3.31017E-02	7.53547E-06
3.95661E-02	9.32007E-06
5.95716E-02	1.43036E-05
7.26364E-02	1.77612E-05
8.57693E-02	2.10583E-05
9.88342E-02	2.43107E-05
1.12103E-01	2.72865E-05
1.18499E-01	2.92273E-05
1.31768E-01	3.24128E-05
1.44901E-01	3.54957E-05
1.51638E-01	3.70929E-05
1.58238E-01	3.85920E-05
1.97025E-01	4.75953E-05
2.63029E-01	6.17784E-05
2.96304E-01	6.93495E-05
3.29510E-01	7.59570E-05
3.94494E-01	8.95869E-05
4.60567E-01	1.02659E-04
5.26436E-01	1.15249E-04
5.92100E-01	1.28460E-04
6.58105E-01	1.40466E-04
7.23633E-01	1.52597E-04
7.89638E-01	1.63799E-04
8.55166E-01	1.75288E-04
9.21171E-01	1.86700E-04
1.00010E+00	1.99554E-04
1.05243E+00	2.09632E-04
1.08571E+00	2.15638E-04

FSG / C_2H_6
40°C

pressure (atm)	moles ads.
3.92289E-03	7.58455E-07
6.55211E-03	1.78014E-06
1.19958E-02	6.15687E-07
1.45816E-02	1.88721E-06
1.73714E-02	2.89551E-06
2.00933E-02	4.28304E-06
2.39720E-02	5.74641E-06
2.77145E-02	7.53993E-06
3.30901E-02	9.81083E-06
3.96225E-02	1.23896E-05
5.92879E-02	2.01749E-05

FSG / C_3H_8
150°C

pressure (atm)	moles ads.
7.51974E-04	3.56920E-08
1.09487E-03	6.24610E-08
1.39013E-03	1.02614E-07
4.29711E-03	4.86303E-07
6.88697E-03	8.16454E-07
9.67684E-03	1.16445E-06
1.23307E-02	1.57937E-06
1.49845E-02	1.98983E-06
1.77743E-02	2.32890E-06
2.04282E-02	2.74382E-06
2.45109E-02	3.37289E-06

7.26249E-02	2.57518E-05
8.48051E-02	3.10654E-05
9.89587E-02	3.60311E-05
1.11888E-01	4.12867E-05
1.18760E-01	4.37048E-05
1.31689E-01	4.80548E-05
1.44890E-01	5.28866E-05
1.51558E-01	5.53583E-05
1.58159E-01	5.77719E-05
1.96877E-01	7.10940E-05
2.62950E-01	9.20273E-05
2.96020E-01	1.02922E-04
3.29295E-01	1.13563E-04
3.94687E-01	1.32609E-04
4.60487E-01	1.50901E-04
5.26220E-01	1.69425E-04
5.92429E-01	1.87187E-04
6.58025E-01	2.04216E-04
7.23758E-01	2.21143E-04
7.89490E-01	2.38070E-04
8.55427E-01	2.53627E-04
9.22384E-01	2.69158E-04
9.99956E-01	2.87584E-04
1.05262E+00	3.00660E-04
1.08569E+00	3.08414E-04

2.85937E-02	3.74766E-06
3.39012E-02	4.57303E-06
4.09100E-02	5.75533E-06
6.19362E-02	8.23592E-06
7.43887E-02	9.89560E-06
8.78617E-02	1.14794E-05
1.01063E-01	1.31659E-05
1.14400E-01	1.50799E-05
1.20388E-01	1.61015E-05
1.34337E-01	1.78505E-05
1.47402E-01	1.96395E-05
1.53458E-01	2.07147E-05
1.60059E-01	2.13170E-05
2.02723E-01	2.59347E-05
2.70974E-01	3.35371E-05
3.00233E-01	3.68297E-05
3.33304E-01	4.06219E-05
4.02507E-01	4.73409E-05
4.67831E-01	5.37120E-05
5.33699E-01	5.98242E-05
5.99432E-01	6.59989E-05
6.65437E-01	7.17275E-05
7.31101E-01	7.75051E-05
7.96902E-01	8.27251E-05
8.62770E-01	8.75257E-05
9.28571E-01	9.22504E-05
1.00887E+00	9.76666E-05

FSG / C_3H_8
125°C

pressure (atm)	moles ads.
7.49868E-04	2.67690E-08
1.09211E-03	4.01535E-08
1.39355E-03	6.24610E-08
4.17118E-03	5.79995E-07
6.81961E-03	1.08861E-06
9.60947E-03	1.50352E-06
1.22633E-02	1.99429E-06
1.48489E-02	2.65459E-06
1.76389E-02	3.07397E-06
2.02926E-02	3.56027E-06
2.43074E-02	4.34550E-06
2.83221E-02	5.12180E-06
3.43783E-02	6.33086E-06

FSG / C_3H_8
75°C

pressure (atm)	moles ads.
7.02895E-04	2.94459E-07
1.07987E-03	4.68457E-07
1.32276E-03	5.62149E-07
3.94184E-03	2.20398E-06
6.53447E-03	3.84581E-06
9.18829E-03	5.75087E-06
1.21142E-02	7.65593E-06
1.51083E-02	9.37807E-06
1.73538E-02	1.06674E-05
2.00076E-02	1.20773E-05
2.38182E-02	1.42902E-05
2.77649E-02	1.63782E-05
3.32766E-02	1.91443E-05

4.05024E-02	7.63362E-06
6.14605E-02	1.16757E-05
7.41851E-02	1.41474E-05
8.79986E-02	1.67975E-05
1.00995E-01	1.94075E-05
1.12767E-01	2.15892E-05
1.20320E-01	2.32756E-05
1.34066E-01	2.55778E-05
1.45906E-01	2.81476E-05
1.53459E-01	2.98296E-05
1.59991E-01	3.08602E-05
2.01840E-01	3.80253E-05
2.69477E-01	4.88579E-05
2.99690E-01	5.40555E-05
3.32692E-01	5.98198E-05
4.01214E-01	7.00544E-05
4.66811E-01	7.95485E-05
5.32611E-01	8.92166E-05
5.98412E-01	9.84429E-05
6.64213E-01	1.07085E-04
7.30013E-01	1.15727E-04
7.95882E-01	1.23682E-04
8.61682E-01	1.31543E-04
9.27551E-01	1.38721E-04
1.00764E+00	1.47046E-04

3.95368E-02	2.25796E-05
5.93382E-02	3.28366E-05
7.26753E-02	3.97207E-05
8.58082E-02	4.61453E-05
9.88049E-02	5.21995E-05
1.11938E-01	5.84099E-05
1.18674E-01	6.15597E-05
1.31807E-01	6.72348E-05
1.44940E-01	7.29053E-05
1.51609E-01	7.57518E-05
1.58209E-01	7.82904E-05
1.96723E-01	9.37985E-05
2.62524E-01	1.18836E-04
2.96206E-01	1.31235E-04
3.28324E-01	1.42478E-04
3.94261E-01	1.65169E-04
4.60470E-01	1.86624E-04
5.26338E-01	2.07031E-04
5.92003E-01	2.26765E-04
6.57939E-01	2.46002E-04
7.23740E-01	2.64170E-04
7.89472E-01	2.82506E-04
8.55273E-01	3.00165E-04
9.21141E-01	3.17123E-04
9.99939E-01	3.36812E-04
1.05261E+00	3.49813E-04

ZSM5 / DME
200°C

pressure (atm)	moles ads.
4.42105E-05	4.33211E-06
7.01316E-05	8.18239E-06
1.29342E-04	2.61444E-05
1.52368E-04	2.97939E-05
2.72895E-04	4.96208E-05
4.06184E-04	6.32150E-05
5.37500E-04	8.35371E-05
6.79079E-04	1.04114E-04
8.00921E-04	1.99835E-04
1.14039E-03	2.58441E-04
1.36711E-03	3.49554E-04
4.71289E-03	4.73003E-04

ZSM5 / DME
175°C

pressure (atm)	moles ads.
4.63158E-05	4.59534E-06
7.48684E-05	8.56607E-06
1.08816E-04	2.39136E-05
1.43553E-04	4.57973E-05
2.71447E-04	1.10797E-04
4.08947E-04	1.85906E-04
5.36842E-04	2.34505E-04
6.66842E-04	4.17694E-04
8.65526E-04	4.48550E-04
1.07447E-03	4.77960E-04
1.32895E-03	4.96203E-04
3.99974E-03	5.61292E-04

6.62842E-03	4.97930E-04	6.62500E-03	5.84844E-04
9.41895E-03	5.23481E-04	9.89053E-03	6.01686E-04
1.24130E-02	5.43129E-04	1.18638E-02	6.09869E-04
1.46584E-02	5.55751E-04	1.45176E-02	6.32324E-04
1.71762E-02	5.67212E-04	1.79199E-02	6.45373E-04
2.05104E-02	5.81967E-04	2.09820E-02	6.56897E-04
2.40488E-02	5.90823E-04	2.36358E-02	6.66815E-04
2.79275E-02	6.02204E-04	2.77866E-02	6.75961E-04
3.39155E-02	6.18627E-04	3.30942E-02	6.89631E-04
4.00396E-02	6.28219E-04	3.94905E-02	7.02463E-04
5.94328E-02	6.57361E-04	5.97003E-02	7.34309E-04
7.30420E-02	6.72870E-04	7.26970E-02	7.55822E-04
8.46779E-02	6.87285E-04	8.64424E-02	7.72330E-04
9.92397E-02	6.99474E-04	9.94391E-02	7.90988E-04
1.12305E-01	7.12220E-04	1.12164E-01	8.05559E-04
1.18565E-01	7.19434E-04	1.18968E-01	8.15379E-04
1.32514E-01	7.27510E-04	1.31965E-01	8.27875E-04
1.45307E-01	7.41206E-04	1.45030E-01	8.44669E-04
1.52792E-01	7.43308E-04	1.52515E-01	8.49616E-04
1.58644E-01	7.51731E-04	1.58299E-01	8.59963E-04
1.98927E-01	7.72829E-04	1.97561E-01	8.90742E-04
2.65068E-01	8.11404E-04	2.63702E-01	9.39913E-04
2.98887E-01	8.24761E-04	2.95003E-01	9.68448E-04
3.30120E-01	8.45846E-04	3.30728E-01	9.87985E-04
3.98710E-01	8.67917E-04	3.96800E-01	1.02805E-03
4.63150E-01	9.01486E-04	4.62669E-01	1.06720E-03
5.32081E-01	9.19921E-04	5.29422E-01	1.10129E-03
5.96248E-01	9.44994E-04	5.95427E-01	1.13379E-03
6.61096E-01	9.74900E-04	6.61363E-01	1.16515E-03
7.30095E-01	9.89382E-04	7.27708E-01	1.19330E-03
7.94534E-01	1.00884E-03	7.93373E-01	1.22188E-03
8.60403E-01	1.02852E-03	8.60262E-01	1.24449E-03
9.26339E-01	1.04742E-03	9.25246E-01	1.27089E-03
1.00412E+00	1.07993E-03	1.00588E+00	1.29721E-03

ZSM5 / DME
150°C

pressure (atm)	moles ads.
5.44737E-05	4.12242E-06
8.50000E-05	7.87900E-06
1.16316E-04	1.18230E-05
1.42895E-04	2.22763E-05
2.72237E-04	2.98349E-04
4.71579E-04	3.60427E-04

5.28684E-04	4.92518E-04
7.49868E-04	5.22209E-04
8.02237E-04	5.44129E-04
1.11118E-03	5.64295E-04
1.34395E-03	5.78513E-04
4.34605E-03	6.28210E-04
6.61132E-03	6.47189E-04
9.74145E-03	6.63590E-04
1.25993E-02	6.76983E-04
1.46408E-02	6.83675E-04
1.75667E-02	6.94410E-04
1.97442E-02	7.02498E-04
2.47116E-02	7.15945E-04
2.79778E-02	7.25141E-04
3.39659E-02	7.41929E-04
3.94776E-02	7.54247E-04
5.88026E-02	7.95507E-04
7.28201E-02	8.19831E-04
8.62933E-02	8.44441E-04
9.79972E-02	8.66833E-04
1.12015E-01	8.85911E-04
1.18071E-01	8.99416E-04
1.31680E-01	9.16610E-04
1.43520E-01	9.37673E-04
1.52638E-01	9.46944E-04
1.57742E-01	9.59267E-04
1.98093E-01	1.00403E-03
2.63281E-01	1.07432E-03
2.96964E-01	1.10417E-03
3.30715E-01	1.13485E-03
3.95631E-01	1.18913E-03
4.61227E-01	1.23066E-03
5.28320E-01	1.27352E-03
5.92420E-01	1.30934E-03
6.58152E-01	1.34073E-03
7.24974E-01	1.37180E-03
7.91386E-01	1.39950E-03
8.57391E-01	1.42510E-03
9.23872E-01	1.44762E-03
1.00172E+00	1.48128E-03

APPENDIX C
BORLAND C++ PROGRAM FOR SIMPLEX DATA ANALYSIS

```
/* Bigfit Program
Revision: 12-10-96
Comments: None   */

#include <stdio.h>
#include <stdlib.h>
#include <math.h>
#include <errno.h>

#define MAXNTEMP 10
#define MAXNSITE 5
#define MAXNPOINT 200
#define MAXFILELINELEN 320



double cal();
double funk();
double _huge b[MAXNTEMP][MAXNPOINT],h[MAXNTEMP][MAXNPOINT];
double _huge p[MAXNTEMP*2*MAXNSITE];
double _huge
dup[MAXNTEMP*2*MAXNSITE],tempup[MAXNTEMP*2*MAXNSITE];
double _huge
ddown[MAXNTEMP*2*MAXNSITE],tempdwn[MAXNTEMP*2*MAXNSITE];
double _huge dif[MAXNTEMP][MAXNPOINT],hh[MAXNTEMP][MAXNPOINT];
double _huge sd[MAXNTEMP][MAXNSITE][2];
double _huge plim[MAXNPOINT];
double _huge avge[MAXNTEMP],ge[MAXNTEMP];
double _huge s[MAXNTEMP*2*MAXNSITE][MAXNTEMP*2*MAXNSITE + 1];
double _huge ri[MAXNTEMP*2*MAXNSITE],tt[MAXNTEMP*2*MAXNSITE];
double _huge c[MAXNTEMP*2*MAXNSITE];
long int _huge ne[MAXNTEMP],n[MAXNTEMP],ns[MAXNTEMP];

main()
{
        char infile[60], outfile[60], tempfile[60];
        char line[MAXFILELINELEN];
        double   per,ep,devn,b1,hcal,bound;
        long int i,is,j,k,nt,ip,kx,tet,tep,tes,z,true;
        long int fixedn, loopz;
        long int total_np,maxns,tot_n,l1,l2;
        FILE *fp;
```

```
        printf("Name of Data File? ");
        scanf(" %s",infile);
        printf("Name of Output File? ");
        scanf("  %s",outfile);
        printf("Name of Working Data File? ");
        scanf(" %s",tempfile);
        loopz=0;
        z=0;
        true=1;
        goto lable400;
lable400:
        if(z == 0){
        if ((fp=fopen(infile,"r"))==NULL)      {
                printf("Sorry. Unable to read from file %s. Exiting.\n",infile);
                exit(0);
        }   }
        else {
        if ((fp=fopen(tempfile,"r"))==NULL)      {
        printf("Sorry. Unable to read from file %s. Exiting.\n",infile);
        exit(0);
        }   }
/*get accuracy bound, max iterations*/
        getfileline(fp,line);
        sscanf(line,"%lg %ld %ld",&ep, &kx, &fixedn);
        printf("line=%s ep=%1.15lf kx=%ld fixedn=%ld\n",line,ep,kx,fixedn);

/* get number of temperature sets*/
        getfileline(fp,line);
        sscanf(line," %ld %ld %lg",&nt,&loopz,&bound);
        printf("\nNumber of temperature sets--> %ld\n",nt);
        tet=MAXNTEMP;
        printf("Max number temperature sets allowed %d\n",tet);
        if (nt > tet)     {
                printf("Sorry. You asked for %ld temperature sets. The maximum number
is %ld.\n",nt,tet);
                exit(0);
        }

        ip = 0;

/* max number of sites*/
        maxns = 0;

/* total number of points*/
        tot_n = 0;
```

```
        for(k=0; k<nt; k++)    {
                avge[k] = 0.0;

/* get number of data points (pressure ratio, moles abs)*/
                getfileline(fp,line);
                sscanf(line," %ld %lf",&(ne[k]),&(ge[k]));
                tep=MAXNPOINT;
                printf("\nMAXNumber of points-->%ld\n",tep);
                printf("number of points-->%ld\n",ne[k]);
                if (ne[k] > tep)  {
                        printf("Sorry. You asked for %ld data points. The maximum
number is %d.\n",ne[k],tep);
                        exit(0);
                }
                n[k] = ne[k];
                tot_n += n[k];

/* read the data points*/
                for(i=0; i<n[k]; i++)   {
                        getfileline(fp,line);
                        sscanf(line," %lf %lf",&(b[k][i]),&(h[k][i]));

                }

/* get the number of sites for this temp set*/
                getfileline(fp,line);
                sscanf(line," %ld",&(ns[k]));
                tes=MAXNSITE;
                printf("max number of sites--->%d\n",tes);
                printf("number of sites%ld\n",ns[k]);
                if (ns[k] > tes)   {
                        printf("Sorry. You asked for %ld sites. The maximum number is
%d.\n",ns[k],tes);
                        exit(0);
                }
                if (ns[k] > maxns)     {
                        maxns = ns[k];
                }
                for(i=0; i<2*ns[k]; i++)      {
                        getfileline(fp,line);
                        sscanf(line," %lf %lf %lf",&(p[ip]),&(ddown[ip]),&(dup[ip]));
                        tempup[ip]=dup[ip];
                        tempdwn[ip]=ddown[ip];
                if(bound != 0){
                  if(z>0){
```

```
                if (tempup[ip] != 0){
                        ddown[ip]=p[ip]*bound;
                        dup[ip]=p[ip]*bound;}}}
                        ip++;
                }
                for(i=0; i<n[k]; i++)   {
                        avge[k] += h[k][i] / ne[k];
                }
                if (avge[k] == 0.0)
                        avge[k] = 1.0;
                for(i=0; i<n[k]; i++)   {
                        hh[k][i] = h[k][i] / ge[k];
                }
                for(i=0; i<MAXNSITE; i++)       {
                        sd[k][i][0] = 0.0;
                        sd[k][i][1] = 0.0;
                }
        }
        fclose(fp);
        total_np = ip;
        if (fixedn)     {

/* same n's for diff temps, so the rest of the n's are dummies
        They should not be variable*/
                for(i=2*maxns; i<total_np; i+=2)        {
                        ddown[i] = 0.0;
                        dup[i] = 0.0;

                }
        }

/* Do the fitting now*/
        printf("WORKING\n");
        simplex(nt,ep,total_np,n,kx,p,ddown,dup,hh,b,ns,maxns,fixedn);

/* All done */

        if ((fp=fopen(outfile,"w"))==NULL)      {
                printf("Sorry. Unable to write to file %s (errno=%d). Exiting.\n",
                        outfile,errno);
                /*scanf(" %s",line);*/
                exit(0);
        }

/*doflag(10);*/
```

```
        ip = 0;
        for(k=0; k<nt; k++)    {
                devn = 0.0;
                for(i=0; i<n[k]; i++)  {
                        dif[k][i] = h[k][i] - ge[k] * cal(k,i,ip,p,b,n,ns,maxns,fixedn);
                }
                for(i=0; i<n[k]; i++)  {
                        devn = pow(dif[k][i],2.0);
                        for(is=0; is<ns[k]; is++)      {
                                if (!fixedn)      {
                                        l1 = ip + 2*is;
                                }
                                else   {
                                        l1 = 2*is;
                                }
                                l2 = ip + 2*is + 1;
                                b1 = p[l2]*b[k][i];
                                if (!fixedn)   {
                                        sd[k][is][0] += pow(((1.0+b1)/b1),2.0)*devn;
                                }
                                else   {
                                        sd[0][is][0] += pow(((1.0+b1)/b1),2.0)*devn;
                                }
                                sd[k][is][1] += pow((dif[k][i]/((p[l1]*b[k][i])-
(dif[k][i]*b[k][i]))),2.0);
                        }
                }
                ip += 2*ns[k];
        }

/*doflag(20);*/
        ip = 0;
        for(k=0; k<nt; k++)    {
                for(is=0; is<ns[k]; is++)  {
                        if (!fixedn)   {
                                l1 = ip + 2*is;
                        }
                        else   {
                                l1 = 2*is;
                        }
                        l2 = ip + 2*is + 1;
                        if (!fixedn)      {
                                sd[k][is][0] = sqrt(sd[k][is][0]/(n[k]-1));
                                if ((ddown[l1]==0.0) && (dup[l1]==0.0))
                                        sd[k][is][0] = -1.0;
```

```
                    }
                    sd[k][is][1] = sqrt(sd[k][is][1]/(n[k]-1));
                    if ((ddown[l2]==0.0) && (dup[l2]==0.0))
                        sd[k][is][1] = -1.0;
                }
                ip = ip + 2*ns[k];
        }

/*doflag(30);*/
        if (fixedn)  {
                for(is=0; is<maxns; is++)  {
                    l1 = 2*is;
                    sd[0][is][0] = sqrt(sd[0][is][0] / (tot_n-1));
                    if ((ddown[l1] == 0.0) && (dup[l1] == 0.0))
                        sd[0][is][0] = -1.0;
                }
        }
        ip = 0;

/*doflag(40);*/
        for(k=0; k<nt; k++)    {
                fprintf(fp,"\nData for temperature set %ld\n",k+1);
                if (ne[k] > 0)
                    fprintf(fp," #  REL PRESS   MOLS ADS       CAL ADS
ERR     PER\n");
                for(i=0; i<n[k]; i++)  {
                    hcal = ge[k] * cal(k,i,ip,p,b,n,ns,maxns,fixedn);
                    per = fabs(100.0 * dif[k][i] / hh[k][i]);
                    fprintf(fp,"%3ld %12.5lE %12.5lE %16.5lE %17.5lE %-10.5lg\n",
                        i+1,b[k][i],h[k][i],hcal,dif[k][i],per);
                }
                for(is=0; is<ns[k]; is++)      {
                    if (!fixedn)      {
                        l1 = ip + 2*is;
                    }
                    else  {
                        l1 = 2*is;
                    }
                    l2 = ip + 2*is + 1;
                    if (!fixedn)      {
                        if(p[l1] < 0)
                        p[l1] = p[l1]*(-1);
                        fprintf(fp,"  n%1ld is %.5lE with a stand. dev. of %.5lE in
mole/g\n",
                                is+1,p[l1],sd[k][is][0]);
```

```
                        if(p[l2] <0)
                        p[l2] = p[l2]*(-1);
                        fprintf(fp,"  K%1ld is %.5lE with a stand. dev. of %.5lE in
mole/g\n",
                                is+1,p[l2],sd[k][is][1]);
                }
                else  {
        if(p[l2] <0)
                        p[l2] = p[l2]*(-1);
                        fprintf(fp,"  K%1ld is %.10lE with a stand. dev. of %.10lE
in mole/g\n",
                                is+1,p[l2],sd[k][is][1]);
                }
        }
        if (ne[k] > 0)
                fprintf(fp,"  Grams of Solid for equilibrium data is
%3.5lg.\n",ge[k]);
        ip += 2*ns[k];
    }

/*doflag(50);*/
    if (fixedn)  {
        for(is=0; is<maxns; is++)     {
                l1 = 2*is;
        if(p[l1] < 0)
                        p[l1] = p[l1]*(-1);
                fprintf(fp,"  n%ld is %.5lE with a stand. dev. of %.5lE in
mole/g\n",
                        is+1,p[l1],sd[0][is][0]);
        }
    }

/*doflag(60);*/
    fclose(fp);
    ip=0;
    if ((fp=fopen(tempfile,"w"))==NULL)     {
        printf("Sorry. Unable to read from file %s. Exiting.\n",infile);
        exit(0);
    }
     fprintf(fp,"# number of loops = %ld\n",z);
     fprintf(fp,"# Convergence Criteria\n");
     fprintf(fp,"%.2le %ld %ld\n",ep, kx, fixedn);
     fprintf(fp,"# number of temperature sets loops bound\n");
     fprintf(fp,"%ld %ld %lg\n",nt,loopz,bound);
     for(k=0; k<nt; k++)   {
```

```
fprintf(fp,"# Data points, grams solid\n");
        fprintf(fp,"%ld %.5lg\n",(ne[k]),(ge[k]));
        fprintf(fp,"#  P/Po   moles ads/g solid\n");
for(i=0; i<n[k]; i++)   {
         fprintf(fp,"%.6le %.6le\n",(b[k][i]),(h[k][i]));
         }
         fprintf(fp,"# number of sites\n");
                fprintf(fp,"%ld\n",(ns[k]));
          for(i=0; i<2*ns[k]; i++)      {
          if(tempup[ip]==0)
                   dup[ip]=tempup[ip];
          if(tempdwn[ip]==0)
                        ddown[ip]=tempdwn[ip];
          if(p[ip]<0)
                p[ip]=p[ip]*(-1);
           ddown[ip]=p[ip]*bound;
                dup[ip]=p[ip]*bound;
          fprintf(fp,"   %.5le       %.5le       %.5le\n",(p[ip]),(ddown[ip]),(dup[ip]));
                ip++;
         }
         }

         fclose(fp);
         z=z+1;
         printf("z = %ld",z);
         printf("z = %ld",loopz);
         if(z<loopz)
         goto lable400;

return 0;
          }


/*
CCCC
```

```
long int nt,n[MAXNTEMP],ns[MAXNTEMP],maxns,fixedn;
{

        double f,b1,fu;
        long int i,k,is,l,ip,n_tot,l1,l2;

        fu = 0.0;
        n_tot = 0;
        ip = 0;
        for(k=0; k<nt; k++)     {
                for(i=0; i<n[k]; i++) {
                        f = 0.0;
                        for(is=0; is<ns[k]; is++)       {

/*  It appears:
c   P(ip+1) = the K(IS)
c   P(ip) = the n(IS) */

                                if (!fixedn)    {
                                        l1 = ip + 2*is;
                                }
                                else    {
                                        l1 = 2*is;
                                }
                                l2 = ip + 2*is + 1;

                                b1 = p[l1]*p[l2]*b[k][i]/(1.0+p[l2]*b[k][i]);
                                f += b1;
                        }
                        fu += pow((h[k][i]-f),2.0);
                }
                ip = ip + 2*ns[k];
                n_tot = n_tot + n[k];
        }
        fu = sqrt(fu/(n_tot-1));
        return fu;
}


/*
CCCC
```

```
CCCC
```

```
C     FUNK=0.0
C     DO 10 I=1,N
C     FUNCTION=function you wish to solve parameters for
C     FUNK=FUNK+(H(I)-FUNCTION) ^ 2
C   10 CONTINUE
C     FUNK=SQRT(FUNK/(N-1))
C     RETURN
C     END
C
C   This function is where the function that you wish to
C   solve the parameters for will go in.
C
C   Attach this function to the main part of the program
C   that you write for input and output of your data
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
*/

simplex(nt,ep,np,n,kx,t,ddown,dup,h,b,ns,maxns,fixedn)
long int nt,np,n[MAXNTEMP],ns[MAXNTEMP],kx,maxns,fixedn;
double
ep,h[MAXNTEMP][MAXNSITE],b[MAXNTEMP][MAXNSITE],t[MAXNTEMP*2*M
AXNSITE];
double ddown[MAXNTEMP*2*MAXNSITE],dup[MAXNTEMP*2*MAXNSITE];
{

        double  br,wr,pr,f,rt,r;
        long int ki,jw,jb,i,j,nv,q;
        q=0;
        br = 0.0;
        parmat(nt,np,t,ri,ddown,dup,b,h,n,ns,maxns,fixedn);
        nv = np + 1;
        if (ri[0] == 0.0)       {
                printf("flag1\n");
                goto lable1 10;
        }
        ki = 0;

/* BR is undefined here!!!! - so I have defined it to be 0.0-- ggh*/

lable10:
        if ((br == 0.0) || (br >= ep))
                goto lable20;
        ep = ep/10.0;
```

```
        goto lable10;

lable20:
        wr = ri[0];
        br = wr;
        jw = 0;
        jb = 0;
        for(i=1; i<nv; i++)    {
                if (ri[i] >= wr)       {
                        wr = ri[i];
                        jw = i;
                }
                if (ri[i] < br) {
                        br = ri[i];
                        jb = i;
                }
        }
        printf("br=%.10lE\n",br);
        if (ki >= kx)  {
                goto lable110;
        }
        if (br < ep)   {
                printf("Best Test withing acceptable limits.\n");
                goto lable110;
        }
        if (((wr-br)/br) < ep)  {
                printf("Unable to improve best test by more than acceptable limits.\n");
                printf("Worst test=%.10lE, Best test=%.10lE, Acceptable
limit=%.10lE\n",wr,br,ep);
                goto lable110;
        }
        ki++;
        if (br != pr)
                pr = br;
        f = 1.0;
        vertix(nt,t,jw,np,f,h,b,&r,n,ns,maxns,fixedn);
        if (r > br)
                goto lable40;
        rt = r;
        for(i=0; i<np; i++)    {
                tt[i] = t[i];
        }
        f = 2.0;
        vertix(nt,t,jw,np,f,h,b,&r,n,ns,maxns,fixedn);
        if (r > rt)
```

```
                goto lable60;

lable90:
        for(i=0; i<np; i++)     {
                s[i][jw] = t[i];
        }
        ri[jw] = r;
        goto lable20;

lable60:
        r = rt;
        for(i=0; i<np; i++)     {
                t[i] = tt[i];
        }
        goto lable90;

lable40:
        if (r <= wr)
                goto lable90;
        f = -0.5;
        vertix(nt,t,jw,np,f,h,b,&r,n,ns,maxns,fixedn);
        if (r <= wr)
                goto lable90;
        for(i=0; i<np; i++)       {
                for(j=0; j<nv; j++)     {
                        if (j != jb)
                                s[i][j] = (s[i][jb] + s[i][j])/2.0;
                }
        }
        goto lable20;
lable110:
        q=q+1;
        if (ki >= kx)
                printf("MAXIMUM NUMBER OF LOOPS EXCEEDED\n");
        else
                printf("CONVERGENCE CRITERIA REACHED\n");
        return;
}


/*
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C
```

```
C   Set up of parameter matrix
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
*/

parmat(nt,np,t,ri,ddown,dup,b,h,n,ns,maxns,fixedn)
long int nt,np,n[MAXNTEMP],ns[MAXNTEMP],fixedn,maxns;
double t[MAXNTEMP*2*MAXNSITE];
double ri[MAXNTEMP*2*MAXNSITE],ddown[MAXNTEMP*2*MAXNSITE];
double
dup[MAXNTEMP*2*MAXNSITE],b[MAXNTEMP][MAXNPOINT],h[MAXNTEMP][
MAXNPOINT];
{
        long int nv,i,j;
        double r;
        nv = np + 1;
        for(i=0; i<np; i++)     {
                for(j=0; j<nv; j++)     {
                        if (i >= j)     {
                                s[i][j] = t[i] + dup[i];

                        }
                        else    {
                                s[i][j] = t[i] - ddown[i];

                        }
                }
        }
        for(i=0; i<nv; i++)     {
                for(j=0; j<np; j++)     {
                        t[j] = s[j][i];
                }
                ri[i] = funk(h,t,b,n,nt,ns,maxns,fixedn);
        }
        return;
}



/*
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCC
C
```

```
C  Find a new vertrix
C
CCCC
```

```
lable10:
        fgets(buf,MAXFILELINELEN,fp);

/*search for first non-whitespace character. If not found, ignore line.*/
        for(i=0; ((buf[i])&&(isspace(buf[i]))); i++);

/*also, lines beginning with a '#' are comments. Ignore them as well*/
        if ((buf[i] == 0) || (buf[i] == '#'))  {
                goto lable10;
        }
        return;
}
```

Example Input Data File for Analysis of Multiple Temperature Adsorption Data

To obtain the adsorption parameters for a particular probe examined at one temperature or at multiple temperatures, the following data file is generated and given a name ?.dat. The program requires the name of an output file which can be called ?.out, and a working file called ?.dxt. When the data fit is finished you can read the output file which will have the parameters at the multiple temperatures listed as well as the error in those parameters.
Happy Hunting...JMM

represents a comment line which will not be read by the program

Bigfit fitting routine for CH4 adsorption by ZSM5 (CBV5020) dried 200oC

# convergence criteria	number of iterations	fix n's to first temperature set value
1e-12	60000	1*

*(use 0 if you want all temp. sets n's to be optimized)

number of temperature sets, number of loops you want the program to make, bounds on the parameters (usually 10 % to start then reduce to 1%)
4 5 .01 (do not under line values in actual data file)

(The data is collected as unsmoothed data, in pressure (torr) and volume adsorbed (cc/g), and is copied from the instrument's computer and changed to pressure in atmospheres by dividing the pressure in torr by 760, and the volume adsorbed is converted to moles adsorbed by dividing by 22414 mL / mole)

rel press moles ads/g solid

0oC
points g solid
26 1.0

3.39087E-02 8.37735E-05
3.91483E-02 9.65290E-05
5.90178E-02 1.44138E-04
7.20825E-02 1.74650E-04
8.52834E-02 2.04426E-04
9.90288E-02 2.34148E-04
1.11005E-01 2.59396E-04
1.18626E-01 2.75194E-04
1.30466E-01 2.99317E-04
1.45028E-01 3.28130E-04
1.51424E-01 3.40604E-04

1.58093E-01 3.53266E-04
1.96471E-01 4.23173E-04
2.62611E-01 5.31538E-04
2.95274E-01 5.80597E-04
3.28956E-01 6.28304E-04
3.93668E-01 7.12126E-04
4.60762E-01 7.90787E-04
5.26494E-01 8.60087E-04
5.91954E-01 9.23704E-04
6.58095E-01 9.82301E-04
7.23624E-01 1.03570E-03
7.89628E-01 1.08490E-03
8.55156E-01 1.13048E-03
9.21229E-01 1.17306E-03
1.00009E+00 1.22013E-03

number of sites
2
n1 (capacity for n1)
.00199
K1 (equilibrium constant for process 1 at this temp.)
1.278
n2
.0009157
K2
.126

-16oC
31 1.0

1.43414E-02 6.57491E-05
1.76757E-02 8.07263E-05
1.97851E-02 8.95869E-05
2.35957E-02 1.06447E-04
2.80867E-02 1.25747E-04
3.30541E-02 1.46150E-04
3.97225E-02 1.73927E-04
6.02045E-02 2.53123E-04
7.20445E-02 2.96221E-04
8.51774E-02 3.41599E-04
9.87186E-02 3.86660E-04
1.12056E-01 4.28884E-04
1.18316E-01 4.48135E-04

1.31789E-01 4.87945E-04
1.44990E-01 5.24735E-04
1.51250E-01 5.41679E-04
1.57987E-01 5.59842E-04
1.97045E-01 6.56790E-04
2.65023E-01 8.01138E-04
2.95372E-01 8.58053E-04
3.28646E-01 9.15133E-04
3.95331E-01 1.01660E-03
4.60860E-01 1.10306E-03
5.26048E-01 1.17818E-03
5.91712E-01 1.24553E-03
6.57921E-01 1.30569E-03
7.23517E-01 1.35924E-03
7.89386E-01 1.40797E-03
8.55323E-01 1.45210E-03
9.20987E-01 1.49246E-03
1.00006E+00 1.53697E-03

number of sites
2
n1
.0000452
K1
2.309
n2
.00198
K2
.1908

-42oC
35 1.0

3.99776E-03 6.48568E-05
6.66987E-03 1.07018E-04
9.11947E-03 1.43718E-04
1.18413E-02 1.83002E-04
1.45632E-02 2.20434E-04
1.72170E-02 2.55969E-04
2.00068E-02 2.91153E-04
2.37495E-02 3.36629E-04
2.79683E-02 3.85786E-04
3.32079E-02 4.41755E-04
3.96722E-02 5.07076E-04
6.04943E-02 6.87891E-04

7.22663E-02 7.74105E-04
8.51270E-02 8.57022E-04
9.86001E-02 9.34791E-04
1.12005E-01 1.00345E-03
1.17993E-01 1.03185E-03
1.31671E-01 1.09196E-03
1.45008E-01 1.14474E-03
1.51132E-01 1.16697E-03
1.58004E-01 1.19076E-03
1.97675E-01 1.31614E-03
2.67150E-01 1.48273E-03
2.95661E-01 1.53652E-03
3.27779E-01 1.59069E-03
3.95553E-01 1.68735E-03
4.60809E-01 1.76238E-03
5.26814E-01 1.82603E-03
5.91866E-01 1.87914E-03
6.57734E-01 1.92576E-03
7.23671E-01 1.96665E-03
7.89472E-01 2.00253E-03
8.55204E-01 2.03490E-03
9.21141E-01 2.06400E-03
1.00014E+00 2.09494E-03

number of sites
2
n1
.0006779
K1
8.138
n2
.00198
K2
.547

-84oC
40 1.0

5.31447E-04 9.89248E-05
6.58684E-04 1.21607E-04
7.86579E-04 1.43683E-04
1.05000E-03 1.86526E-04
1.30645E-03 2.25346E-04
4.00316E-03 5.48229E-04
6.59776E-03 7.60435E-04

9.18355E-03	9.17418E-04
1.19054E-02	1.05055E-03
1.43550E-02	1.15276E-03
1.69408E-02	1.24123E-03
1.96626E-02	1.32149E-03
2.36092E-02	1.42129E-03
2.75559E-02	1.50098E-03
3.26593E-02	1.59179E-03
3.98722E-02	1.69436E-03
6.06943E-02	1.89512E-03
7.20580E-02	1.97171E-03
8.53951E-02	2.04140E-03
9.80516E-02	2.09565E-03
1.11525E-01	2.14429E-03
1.17785E-01	2.16388E-03
1.31258E-01	2.20256E-03
1.45412E-01	2.23733E-03
1.50855E-01	2.24918E-03
1.57864E-01	2.26385E-03
1.97603E-01	2.33589E-03
2.66261E-01	2.42461E-03
2.95249E-01	2.45345E-03
3.27843E-01	2.48204E-03
3.95345E-01	2.53161E-03
4.60533E-01	2.57088E-03
5.25993E-01	2.60389E-03
5.91862E-01	2.63261E-03
6.57866E-01	2.65786E-03
7.23667E-01	2.68045E-03
7.89536E-01	2.70058E-03
8.55336E-01	2.71869E-03
9.21069E-01	2.73513E-03
1.00000E+00	2.75334E-03

number of sites
2

n1
.000029
K1
85.77
n2
.00198
K2
5.008

APPENDIX D

LIQUID ADSORPTION DATA

Adsorption by Fisher Silica Gel (lot # 934403)

Benzene

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.0282	9.32E-05	4.67778E-05
0.0441	0.000111	7.23198E-05
0.1033	0.000205	0.000162514
0.1513	0.000284	0.000230433
0.2191	0.000349	0.000319299
0.2948	0.000452	0.000409878
0.4004	0.000438	0.000523166
0.4953	0.000552	0.00061393
0.5687	0.000676	0.000677981
0.643	0.000695	0.00073802
0.8362	0.000949	0.000875057

Benzonitrile

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.0003801	1.766E-05	7.17792E-05
0.0003983	5.475E-05	7.49456E-05
0.0005993	5.859E-05	0.000108466
0.0007942	0.0001013	0.000138629
0.001812	0.0002982	0.000267138
0.003812	0.0004616	0.000432758
0.007617	0.0006326	0.000608862
0.0175	0.0008049	0.000819235
0.042	0.001031	0.00104526
0.0788	0.001218	0.00122917
0.1411	0.001435	0.00141507
0.1888	0.001484	0.00150827
0.2938	0.00167	0.00164142
0.4087	0.001778	0.00172939
0.48	0.001736	0.00176781
0.4986	0.001751	0.00177645

Chlorobenzene

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.0209	5.12E-05	4.26403E-05
0.0391	8.99E-05	7.64468E-05
0.0908	0.000167	0.000158733
0.1632	0.00026	0.000248463
0.239	0.000305	0.000320533
0.3208	0.000384	0.000381245
0.4223	0.000443	0.000439734
0.5184	0.000468	0.000483165
0.6042	0.000504	0.0005149
0.6805	0.000562	0.000538877
0.8765	0.000542	0.000587306
1.0566	0.000659	0.000620296

Nitrobenzene

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.0024	0.0002664	0.000170224
0.00465	0.0001568	0.000281547
0.0101778	0.0004931	0.000460084
0.01182	0.0005268	0.000498598
0.0388	0.0008262	0.000841348
0.048675	0.0008752	0.000915608
0.06559	0.0010581	0.00101916
0.123	0.0012767	0.00125868
0.17459	0.00145	0.00139971
0.1994	0.0013635	0.00145316
0.2785	0.0015912	0.00158407
0.3477	0.0016817	0.00166612
0.4094	0.0017266	0.001723
0.60317	0.0018399	0.00184352

p-Xylene

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.001276	3.53E-05	3.02177E-05
0.01392	0.0001186	0.000127124
0.02204	0.0001575	0.000157112
0.02312	0.0001491	0.000160673
0.0334	0.0002108	0.000191832
0.04328	0.0002119	0.000218769
0.07597	0.0003342	0.00029675
0.11697	0.0003531	0.000379493
0.19508	0.000493	0.000506755
0.2518	0.0005947	0.000581231
0.43098	0.0007174	0.000753615
0.44018	0.0007478	0.000760601
0.68196	0.0009183	0.000903708
0.95349	0.0011052	0.00100591
1.33179	0.001026	0.00109658

Pyridine

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.0006801	0.0001405	0.000447524
0.0006949	0.0002667	0.000454491
0.0007103	0.0005443	0.000461651
0.000791	0.000883	0.000497754
0.007189	0.001307	0.00129801
0.03457	0.001599	0.00162015
0.08831	0.001816	0.00181709
0.1657	0.002019	0.00200424
0.2206	0.002132	0.00210726
0.2898	0.002175	0.00221436
0.46	0.002417	0.0024075

Adsorption by Ambersorb 572 (lot# 2201)

Benzene

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.00856	0.0001205	4.01236E-05
0.0118	0.000263	5.51648E-05
0.01222	0.000314	5.71087E-05
0.0582	0.000428	0.000262187
0.0711	0.000427	0.000317094
0.0959	0.000444	0.000419621
0.1558	0.000647	0.000651984
0.163	0.000537	0.000678557
0.2554	0.000647	0.000996509
0.2963	0.0009568	0.00112485
0.397	0.00149	0.00141314
0.4109	0.001655	0.00145013
0.5942	0.001916	0.00188485
0.9185	0.002804	0.00247119
1.315	0.00266	0.00298402
1.684	0.00329	0.00333537
2.046	0.0037	0.00360284

Benzonitrile

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.000332	0.0003502	0.000353517
0.001703	0.0005417	0.000541093
0.004499	0.0007437	0.000692943
0.0135	0.0008629	0.00100472
0.02481	0.001319	0.00124868
0.04184	0.001556	0.00147277
0.113	0.001643	0.00183642
0.132	0.002025	0.00187991
0.2446	0.001976	0.0020147
0.3936	0.001934	0.00208326
0.436	0.002271	0.00209478

Chlorobenzene

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.00043	0.000146	0.000141292
0.00137	0.000269	0.000269951
0.0172	0.000522	0.00055765
0.0469	0.000812	0.000764285
0.0935	0.000999	0.000967251
0.1704	0.0011	0.00116163
0.2518	0.00129	0.00128125
0.3285	0.00137	0.00135486
0.4042	0.00143	0.00140668
0.5068	0.00139	0.00145717
0.687	0.00147	0.00151506
0.8497	0.00163	0.00154899

Nitrobenzene

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.00191	0.000549	0.00045331
0.00445	0.0006566	0.00074046
0.00564	0.000786	0.000829414
0.00831	0.00101	0.000980521
0.023	0.00141	0.0014231
0.048	0.00185	0.00180189
0.0644	0.002	0.00196229
0.108	0.00225	0.00223806
0.198	0.00248	0.00251919
0.264	0.00259	0.00262857
0.632	0.00272	0.00286114
0.825	0.00282	0.00290667
1.026	0.00301	0.00293705
1.033	0.003088	0.00293791
1.345	0.002987	0.00296755

Pyridine

Concentration Equilibrium (moles/L)	Eperimental moles adsorbed	Calculated moles adsorbed
0.0001176	8.41E-05	1.82651E-05
0.0013	0.000152	0.000153089
0.002612	0.0001361	0.000244391
0.003164	0.0002742	0.00027306
0.0035	0.000303	0.000288593
0.003566	0.0004325	0.000291497
0.01375	0.0003509	0.000518261
0.0145	0.000533	0.000528195
0.01952	0.0005844	0.000587075
0.0303	0.000768	0.000689247
0.04846	0.0009086	0.000829801
0.0776	0.00109	0.00101773
0.1316	0.001316	0.00129791
0.1683	0.001285	0.00145391
0.1901	0.001514	0.00153649
0.2393	0.001603	0.00170053
0.2677	0.001834	0.00178343
0.3223	0.001896	0.00192338
0.3602	0.002009	0.00200805
0.3826	0.002047	0.00205402
0.4801	0.002467	0.00222563
0.6602	0.002209	0.00245653
0.9502	0.002907	0.00269523
1.476	0.002988	0.00293607
2.212	0.002985	0.00310806

LIST OF REFERENCES

1. Patrick, John W., "Porosity in Carbons: Characterization and Applications," John Wiley and Sons, New York, 1995.

2. Cronstedt, A. F., *Akad. Handl. Stockholm*, **1756**, *18*, 120.

3. Gregg, S. J. and Sing, K. S. W., "Adsorption, Surface Area, and Porosity," Academic Press, London, 1982.

4. Foley, H. C., *Microporous Materials*, **1995**, *4*, 407-433.

5. Neely, J. W.; Isacoff, E. G. "Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters," Marcel Dekker, New York, 1982.

6. Armor, J. N. *Appl. Catal. B Environmental* **1992**, *1*, 221.

7. Yang, Y., Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1729.

8. a. Drago, R. S.; Burns, D. S. Preparation and Evaluation of Novel Reactive and Catalytic Adsorbents, "Proceedings of the 1993 ERDEC Scientific Conference on Chemical Defense Research," Aberdeen, Maryland, November 1993.

   b. Drago, R. S.; Burns, D. S.; McGilvray, J. M. Porous Solids as Adsorbents and Catalyst Supports. "Proceedings of the 1994 ERDEC Scientific Conference on Chemical Defense Research," Aberdeen, Maryland, November 1994.

   c. Drago, R. S.; McGilvray, J. M.; Kassel, W. S. Fundamental Studies of Porous Solids for Decon and Demil Applications, "Proceedings of the 1995 ERDEC Scientific Conference on Chemical Defense Research," Aberdeen, Maryland, November 1995.

9. Ray, M. S. *Separ. Sci. & Technol.* **1983**, *18(2)*, 95.

10. Sircar, S. *Separ. Sci. & Technol.* **1988**, *23(14&15)*, 2379.

11. Basta, N. *Chemical Engineering* September 26, 1988, p.26.

12. Iler, R. K. "The Chemistry of Silica," Wiley-Interscience, New York, 1979.

13. Breck, D. W. "Zeolite Molecular Sieves: Structure, Chemistry, and Use," John Wiley and Sons, New York, 1974

14. Barrer, R. M. "Zeolites and Clay Minerals as Sorbents and Molecular Sieves," Academic Press, London, 1978.

15. Dyer, A. "Zeolite Molecular Sieves," John Wiley and Sons, London, 1988.

16. Bhatia, Subhash "Zeolite Catalysis: Principles and Applications," CRC Press, Boca Raton, Florida, 1990.

17. a. Sing, K. S. W.; Everett, D. H.; *Pure & Appl. Chem.*, **1985**, 57*(4)*, 603-619.

b. Rouquerol, J.; Faibridge, C. W.; *Pure & Appl. Chem.*, **1994**, *66(8)*, 1739-1758.

18. White, M. G. "Heterogeneous Catalysis," Prentice Hall, Englewood Cliffs, New Jersey, 1990.

19. Israelachvili, J. "Intermolecular & Surface Forces," Academic Press, London, 1991.

20. Kihara, T. "Intermolecular Forces," John Wiley and Sons, New York, 1978.

21. Amarasekera, G.; Scarlett, M. J.; Mainwaring, D. E. *J. Phys. Chem.* **1996**, *100*, 7580.

22. Everett, D. H.; Powl, J. C. *J. Chem. Soc. Faraday Trans. 1*, **1976**, *72*, 619.

23. Langmuir, I. *J. Am. Chem. Soc.*, **1918**, *40*, 1361.

24. Adamson, A. W. "Physical Chemistry of Surfaces," 5th Ed., John Wiley and Sons, New York, **1990**.

25. Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.*, **1938**, *60*, 309.

26. Brunauer, S. *Langmuir* **1987**, *3*, 2.

27. a. Dubinin, M. M.; Radushkevich, L. V. *Proc. Acad. Sci.* USSR. **1947**, *55*, 331.

b. Dubinin, M. M. *Chem. Rev.*, **1960**, 60, 235.

c. Dubinin, M. M. *J. Colloid and Inter. Sci.* **1967**, *23*, 487.

28. Horvath, G.; Kawazoe, K. *J. Chem. Eng. Japan*, **1983**, *16(6)*, 470.

29. Choudhary, V. R.; Mayadevi, S.; Singh, P. *J. Chem. Soc. Faraday Trans.* **1995**, *91(17)*, 2935.

30. Drago, R. S.; Burns, D. S.; Lafrenz, T. J. *J. Phys. Chem.*, **1996**, *100*, 1718.

31. Drago, R. S.; McGilvray, J. M.; Kassel, W. S. *The Micro Report*, **1996**, 7(3).

32. Everett, D. H. *Langmuir* **1993**, *9*, 2586.

33. Gordon, A. J.; Ford, R. A. "The Chemist's Companion," John Wiley and Sons, New York, 1972, p. 451.

34. Harkins, W. D.; Jura, G. *J. Am. Chem. Soc.*, **1944**, *66*, 1366.

35. Barrett, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.*, **1951**, *73*, 373.

36. "Lange's Handbook of Chemistry," 13th Edition; McGraw-Hill, New York, 1985. All data are from this source unless otherwise specified.

a. "Handbook of Chemistry and Physics," 71st Edition; CRC Press: Boca Raton, Florida, 1991.

b. McClellan, A. L. "Tables of Experimental Dipole Moments;" W. H. Freeman and Company, San Fransisco, 1963, p. 123.

c. Molar volume of the liquid at the normal boiling point. Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. "Regular and Related Solutions;" Van Nostrand Reinhold Company: New York, 1970, p.217

d. Breck, D. W. "Zeolite Molecular Sieves," John Wiley & Sons, New York, 1974, p. 636

37. Sing, K. S. W. *Carbon* **1989**, *37(1)*, 5.

38. McClellan, A. L.; Harnsberger, H. F. *J. Colloid Interface Sci.*, **1967**, *23*, 577.

39. Meier, W. M.; Olson, D. H. "Atlas of Zeolite Structures Types," Butterworth-Heinemann, London, 1992.

40. Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.*, **1981**, *85*, 2238.

41. June, R. L.; Bell, A. T.; Theodoro, D. N. *J. Phys. Chem.*, **1990**, *94*, 1508.

42. Smit, B.; Maesen, T. L. *Nature* **1995**, *374*, 42.

43. Stach, H.; Lohse, U.; Thamm, H.; Schirmer, W. *Zeolites* **1986**, *6*, 74.

44. Drago, R. S.; Webster, C. E. *J. Am. Chem. Soc.* submitted.

45. Amari, D.; Ginoux, J. L.; Bonnetain, L. *Zeolites* **1994**, *14*, 58.

46. Adamson, A. W. *Colloids and Surfaces A: Physiochemical and Engineering Aspects* **1996**, *118*, 193.

47. a. Chronister, C.; Drago, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 4793.

b. Lim, Y.; Drago, R. S.; Batich, M.; Wong, N.; Doan, P. *J. Am.Chem. Soc.* **1987**, *109*, 169.

48. Handbook of Chemistry and Physics, 71st Edition; CRC Press, Boca Raton, Florida, 1991.

a. Drago, R.S. *J.Chem. Soc., Perkin Trans. 2*, **1992**, *1827*.

b. Miessler, G. L.; Tarr, D. A. "Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, New Jersey, 1991, pp. 195-197. As well as data from reference 50.

49. Wade, L. G. "Organic Chemistry," Prentice-Hall, Englewood Cliffs, New Jersey, 1987.

50. Drago, R. S. "Applications of Electrostatic and Covalent Models in Chemistry," Surfside Scientific Publishers, Gainesville, Florida, 1994.

51. Misono, M.; Okuhara, J. *Chemtech* **1993**, 23.

52. Guisnet, M. R. *Acc. Chem. Res.* **1990**, *23*, 392.

53. a. Corma, A.; Wojciechowski, B. W. *Catal. Rev. - Sci. Eng.* **1985**, *27(1)*, 29.

b. Corma, A.; Martinez, A. *Catal. Rev. - Sci. Eng.* **1993**, *35(4)*, 483.

54. Pines, H. "The Chemistry of Catalytic Hydrocarbon Conversion," Academic Press, New York, 1981.

55. Field, L. D. Alkane Activation with Superacids In "Selective Hydrocarbon Activation, Principles and Progress," VCH Publishers, New York, 1990.

56. Scott, B. *Hydrcar. Proc.* **1992**, October., *77*.

57. Arata, K. *Adv. Catal.* **1990**, *17*, 165.

58. a. Getty, E.; Drago, R.S. *J. Am. Chem. Soc.* **1988**, *110*, 3312.

b. Getty, E.; Drago, R.S. *Inorg. Chem.* **1990**, *29*, 1186.

c. Drago, R. S.; Petrosius, S.; Chronister, C. *Inorg. Chem.* **1994**, *33*, 367.

59. Kob, N. E. Dissertation University of Florida, 1996

60. Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.

61. Gesser, H. D.; Goswami, P. C. *Chem. Rev.* **1989**, *89*, 765.

62. Buckley, A. M.; Greenblatt, M. *J. Chem. Ed.* **1994**, *71(7)*, 599.

63. Schmidt, H.; Scholze, H.; Kaiser, A. *J. Non-Cryst. Solids* **1984**, *63*, 1.

64. Lev, O.; Tsionsky, M.; Rabinovich, L.; Glezer, V.; Sampath, S.; Pankratov, I.; Gun, J. *Anal. Chem.* **1995**, *67(1)*, 22A.

65. Schneider, M.; Baiker, A. *Catal. Rev. - Sci. Eng.* **1995**, *37(4)*, 515.

66. Brinker, C. J. "Sol-Gel Science: The Physics and Chemistry of the Sol-Gel Process," Academic Press, New York, 1990.

67. Yoldas, B. E. *J. Non-Cryst. Solids* **1986**, *82*, 11.

68. Hench, L. L.; Ulrich, D. R. "Science of Ceramic Chemical Processing," John Wiley and Sons, New York, 1986.

69. Scherer, G. W.; Luong, J. C. *J. Non-Cryst. Solids* **1984**, *63*, 163.

70. Hench, L. L.; Orcel, G. *J. Non-Cryst. Solids* **1986**, *82*, 1.

71. Chujo, Y.; Matsuki, H.; Kuru, S.; Saegusa, T.; Yazawe, T. *J. Chem. Soc., Chem. Commun.* **1994**, p. 635.

72. Brown, J. F.; Vogt, L. H.; Prescott, P. I. *J. Am. Chem. Soc.* **1964**, *86*, 1120.

73. Shea, K. J.; Loy, D. A. *Chem. Mater.* **1989**, *1*, 572.

74. Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700.

75. Oviatt, H. W.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993**, *5*, 943.

76. a. Neumann, R.; Levin-Elad, M. *J. Catal.* **1997**, *166*, 206.

b. Neumann, R.; Chava, M.; Levin, M. *J. Chem. Soc. Chem. Commun.* **1993**, 1685.

77. Feher, F. J.; Walzer, J.F.; Blanski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 3618.

78. Congshen, Z.; Fuxi, G.; Zhonghong, J. *J. Non-Cryst. Solids* **1984**, *63*, 105.

79. Kern, W. *J. Electrochem. Soc.* **1990**, *137(6)*, 1887.

80. a. Corma, A.; Martinez, A.; Martinez, C. *J. Catal.* **1994**, *149*, 52.

b. Corma, A.; Fornes, V.; Juan-Rajadell, M. I.; Lopez Nieto, J. M. *Appl. Catal.* **1994**, *116*, 151.

81. Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry," 5th Ed., John Wiley and Sons, New York, 1988.

82. Greenwood, N. N.; Earnshaw, A. "Chemistry of the Elements," Pergamon Press, New York, 1984.

83. Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, 1963.

BIOGRAPHICAL SKETCH

John Michael McGilvray was born on November 11, 1968, in Mobile, Alabama, to Jeff and Hazel McGilvray. He attended Mobile Christian High School where he was vice-president of the National Honor Society, editor of the school yearbook, and school photographer. He graduated third in his class in 1987.

In September of 1987, he entered the University of South Alabama where, under the direction of Professor Norris W. Hoffman, he studied the effects of carbonylation of iron and ruthenium complexes. He received his Bachelors of Science in Chemistry degree in June of 1992 from South Alabama. He enrolled as a graduate student at the University of Florida in August of 1992, where he worked for Graduate Research Professor Russell S. Drago studying the adsorption properties of various solids and their potential as adsorbents and strong acid catalysts. He was married to Victoria Marie Cooley on June 17, 1995. Mike's plans beyond his doctoral studies are not yet confirmed.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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